A Study on Effect of Temperatures on the Flammability of Biodiesel Vapour Mixtures for Accident Prevention

by

Qurratuaini binti Muhamad Nazori

Dissertation submitted in partial fulfilment of

the requirements for the

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(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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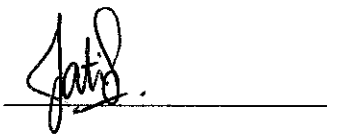
Approved by,



(Dr. Mohanad El-Harbawi)

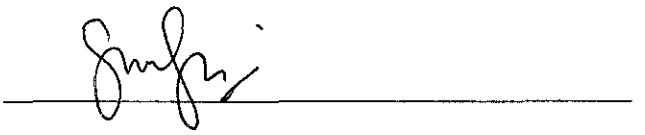
UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



QURRATUAINI BINTI MUHAMAD NAZORI

ABSTRACT

Biodiesels are widely used as an alternative fuel resulting from higher global energy demands as they are environmental friendly. Study on fire and explosion is very important mainly in industrial activities due to previous cases that have been reported involving biodiesel. In general biodiesel is considered to be much safer than fossil fuels as it is much less flammable due to its high flash point. However, biodiesel will combust if it is heated up to over 150°C. Therefore, this study is conducted to investigate the flammability of biodiesel vapor mixtures at different range of temperature varying from 50°C-200°C. Biodiesel produced by chemically reacting lipids with an alcohol via transesterification process was analyzed using Gas Chromatography Mass Spectrometry (GC-MS) to examine the composition of the sample. Total components vaporized from biodiesel sample differ at different temperatures. The results from GC-MS indicated that there are three components vaporized from biodiesel liquid sample at 150°C and six components at 200°C. Mole fractions of components in the vapor phase were calculated using modified Raoult's law. The fugacity coefficients were predicted using ThermoSolver software based on Peng-Robinson method, while the activity coefficients were calculated using COSMO software. Lower Flammability Limit (LFL) and Upper Flammability Limit (UFL) for individual components were calculated using the flammability limit dependence on temperature equation (Zabetakis, S.Lambiris, & Scott, 1959). While LFL and UFL values for the mixture (LFL_{mix} and UFL_{mix}) were determined using Le Chatelier equation (Chatelier, 1891). Limiting Oxygen Concentrations (LOCs) were determined using equation proposed by Hansen and Crowl (Hansen & Crowl, (June 2010)). The LFL_{mix}, UFL_{mix}, and LOC_{mix} values were used to construct the flammability diagram and to determine the flammability of biodiesel vapor mixture at 50°C, 100°C, 150°C and 200°C. From the flammability diagram, it shown that biodiesel vapor mixture is not flammable at lower temperature; 50°C and 100°C but as the temperatures increase; 150°C and 200°C the biodiesel became flammable. The findings of this study may assist in minimizing fire hazards associated with presence of organic compound vapors derived from biodiesel.

ACKNOWLEDGEMENT

Throughout the whole period of conducting the Final Year Project, many have provided immeasurable amount of guidance, ideas, assistance, support and advice. I hereby express my warmest gratitude and appreciation to my supervisor, Dr Mohanad El-Harbawi for the continuous support and encouragement of my final year project, for his valuable suggestions, patience, motivations, enthusiasm, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis.

Also my biggest thanks to the Final Year Project coordinator, Dr Norhayati Mellon and all Chemical Engineering Department lecturers for their cooperation in providing me all the necessary information, references and equipments to conduct this study. My special appreciation also goes to the staff and technicians especially Mr Fauzi who always help me in conducting GC-MS laboratory analysis and to Mr Marwan from UTP research centre for assisting me in the production of biodiesel liquid sample.

Deepest thanks to my family, friends and others who always give their best guidance, cooperation and support throughout these semesters from the beginning of my project until the thesis completion. Last but certainly not the least, I wish everyone the very best and continue to provide excellent guidance and support for innovative research in the future. Thank You.

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LIST OF ABBREVIATIONS

GC-MS – Gas chromatography–mass spectrometry

LFL – lower Flammability Limit

UFL – Upper Flammability Limit

LOC – Limiting Oxygen Concentration

DOT – Department of Transportation

NFPA – National Fire Protection Association

OSHA – Occupational Safety and Health Administration

EPA – Environmental Protection Agency

MSSC – Maximum Safe Solvent Concentration

ASTM – American Society for Testing and Materials

CAFT – Calculated Adiabatic Flame Temperature

MOC – Minimum Oxygen Concentration

AIT – Auto Ignition Temperature

SIT – Spontaneous Ignition Temperature

N_2 – Nitrogen

CHAPTER 1

INTRODUCTION

1.1 Background of Study

As global demand for energy supply is kept increasing, biodiesel are used widely as they are environmental friendly. Fossil fuel reserves such as oil, coal and gas will be exhausted in less than another 10 decades (Sharma & Singh, 2009). Biodiesel refers to a vegetables oil or animal fat-based diesel fuel consisting of long-chain alkyl esters. Biodiesel is typically made by chemically reacting lipids with an alcohol producing fatty acid esters. The process used to produce biodiesel from these oils is called transesterification. In general, biodiesel are considered to be much safer than other energy sources as it is much less flammable than petro-diesel, owing to higher flash point; >130°C. Since biodiesel consist of some organic components, these components therefore will vaporize and turn into vapor mixtures at different range of temperatures and atmospheric pressure. Based on the fire triangle, there are three essential elements for combustion which are fuel, an oxidizer and ignition source. These vapor mixtures from biodiesel lies under fuel category. If these vapor mixtures are exposed to air and ignition sources, and the concentration is between the LFL and UFL, they may burn and lead to the fire and explosion. Therefore, it is necessary to understand the characteristics and properties of these flammable components in biodiesel in order to reduce if not eliminate the risk of fire and explosion incident.

It can be said that flammability limits and related information are crucial in the industrial processes where serious hazards may be encountered within the flammability limits. To address safety issues in the design and operation of chemical plants, an inherent safer design are introduced (Dennis, 2006). This design will identify ways to eliminate or significantly reduce hazard. Therefore biodiesel storage systems and production processes should be designed with systematic and safer

methods to avoid fire and explosion. There have been many fire and explosion incidents in biodiesel plant in the past. Perhaps the worst biodiesel accident occurrence in the past is at Better Biodiesel Spanish Fork, Utah on 2007 involving 11 injuries.

1.2 Problem Statement

The combustion of one gallon of biodiesel can destroy an ordinary chemistry laboratory in minutes and may kill the persons present. Moreover the potential consequences of fires and explosions in biodiesel plant are even greater. The flammability limits are used as an approach to represent flammability of vapor mixture in biodiesel. Since biodiesel are widely used as an alternative fuel resulting from global energy demands, safety precautions have arise due to the possibility of forming flammable mixture found in biodiesel. In addition there have been several cases reported on fire and explosion involving biodiesel. Some components in biodiesel can be vaporized at certain temperatures and will turn into vapor mixtures. If the concentration of these vapor mixtures was identified to be within the flammability range and those were exposed to air and ignition sources, it can lead to fire and explosion. Due to some previous cases on fire and explosion involving biodiesel, this study is aiming to investigate the flammability of biodiesel at different range of temperatures; lower and higher temperature vary from 50°C to 200°C at atmospheric pressure. Finding from this study can be used to propose a systematic and safer approach in the design and operation of biodiesel storage systems and production processes.

1.3 Objectives

The objectives of this study are:

- To estimate the flammability limits and examine the flammability of biodiesel vapor mixture at different range of temperatures.

- To investigate the possibility of fire incidents due to the vaporization of organic components from biodiesel liquid sample.
- To recommend a suitable and systematic safety method in handling biodiesel storage systems and production process areas to eliminate fire and explosion incidents.

1.4 Scope of Study

This study focuses on real solution of biodiesel. This study involves experimental works and theoretical works. Experimental works involved the production of biodiesel from vegetable oil and methanol using transesterification process. Then the composition of biodiesel produced will be analyzed using Gas Chromatography Mass Spectrometry (GC-MS) to identify all the components in liquid biodiesel at different range of temperatures. For theoretical works this study involved the correlation of thermodynamic where the mole fraction of the components in vapor phase will be calculated using modified Raoult's Law. Simulation work was also involved where COSMO software was used to calculate the activity coefficients whereby fugacity coefficients were predicted using ThermoSolver software based on Peng-Robinson method for each component in the biodiesel vapor mixtures at different range of temperatures. All these values will be used to calculate the LFLs, UFLs and LOCs for each component and also LFL_{mix}, UFL_{mix}, and LOC_{mix} for the mixture. Later, LFL_{mix}, UFL_{mix}, and LOC_{mix} will be used to construct the flammability diagram and predict the flammability of biodiesel. Finally the results from this study will be used to propose the suitable inherent safety approach in handling biodiesel storage systems and production processes to eliminate fire and explosion incident.

1.5 Relevancy and feasibility of the project

This study is relevant since it is related to the student with background study of chemical engineering. Furthermore this study focuses on safety of biodiesel as safety is very crucial in handling any flammable chemicals for accident prevention regardless at any places. The knowledge of process safety and loss prevention, thermodynamics, chemicals analysis and health safety environment (HSE) is very much applied in this study. Tools and equipments used for this study are readily available in university laboratory which is in block 4. For accuracy of this study, the data obtained from GC-MS was compared with data from PETRONAS Research Sdn Bhd (PRSB) Bangi. Biodiesel sample was produced in bio oil research laboratory in block 5 UTP. This project is feasible within the scope and time frame.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Energy sources play a significant role in human's life. Currently, most of the energy we use comes from fossil fuels: petroleum, coal and natural gas. While fossil fuels are still being created today by underground heat and pressure, they are being consumed more rapidly than they are being created (Demirbas, 2008). Fossil fuel reserves such as oil, coal and gas will be exhausted in less than another 10 decades (Y.C Sharma, 2009). Figure 2.1 shows the global oil production scenarios based on 2008 production. Because of this rising global energy demand and as the fossil fuels are reducing over time, renewable energy sources (RESs) have been introduced as alternative fuel to fulfill the energy demand of the world. One of the RESs is biodiesel as it is environmental friendly and has many advantages: liquid nature-portability, ready availability, renewability, higher combustion efficiency, lower sulfur and aromatic content, higher cetane number and higher biodegradability. (Balat, 2010). In general, biodiesel is considered safer as it has higher flash point; >130°C compared to petroleum fuels. Thus biodiesel will not easily ignite or produce fire at low temperature. In other word, biodiesel is considered much less flammable than petroleum fuels. However, presences of some organic components in biodiesel liquid expose biodiesel storage tanks and production process areas to fire accidents. If biodiesel is exposed to some heat at higher temperature, some components from biodiesel liquid will vaporize and turn into vapor mixture and if this vapor mixture is exposed to air and ignition sources and the concentration of mixture is within the flammability range it can lead to fire.

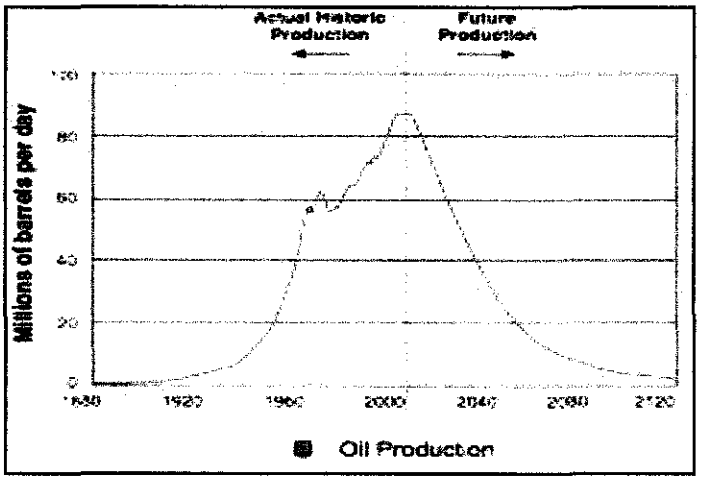

Figure 2.1: Global oil production scenario based on 2008 production.

There are innumerable situations where gases, liquids and hazardous chemicals are produced, stored or used in a process which are having high risk and if released, could potentially result in a hazardous fire and explosion incident. Thus, it is important to analyze all materials and reactions associated with a particular process in biodiesel production, including process reaction, manufacturing, storage or treatment facilities in order to minimize the opportunity for an undesirable situation. Each process needs to be analyzed with respect to the potential for the occurrence of fire and explosion in the work place.

Typically, system accidents occur because of unexpected interaction among multiple failures. One component's failure triggers failures in other components or subsystems. Due to the high complexity and level of interaction among subsystems, designers and operators are unable to predict failures or their mutual interactions.

Previous cases on fire and explosion accidents involving biodiesel have lead this flammability study on biodiesel. Table 2.1 shows a summary of the major incidents in biodiesel process industries related to fire and explosion cases.

Table 2.1: Summary of major incidents involving biodiesel process industries

Year	Plant location	Chemical	Death/Injury
2006	American Biofuels, Bakersfield, California	Methanol	2
2006	Sun Break Biofuels, Canby, Oregon	Ethanol	1
2006	Blue Sky Biodiesel, Idaho	Biodiesel	1
2007	Agri Biofuels Dayton, Texas	Methanol	1
2007	Better Biodiesel Spanish Fork, Utah	Methanol	11
2008	Biofuels of Tennessee Decaturville	Acetone	1
2008	Green Light Biofuels Princess Ann, Maryland	Biofuels	2
2008	All American Biodiesel York, North Dakota	Biodiesel	n/a
2009	Minnesota Soybean Brewster	Biodiesel	n/a
2009	Midwest Biorenewables, Toledo	Biodiesel	n/a
2009	Columbus Foods Company Chicago	Sulphuric acid/glycerin	2
2009	New Eden Energy St. Cloud, Florida	Biodiesel	n/a

Fire and explosion cannot be predicted but can be prevent by understanding the flammability characteristics of those chemicals. The understanding of the flammable properties and characteristics is important and necessary when dealing with hazardous materials. Fire and explosion hazard may be eliminated by knowing the flammability characteristics and related safety approach.

2.2 Fire and Explosion

Three essential elements must be present for fire to occur are fuel, heat and oxygen. All these elements have been illustrates in figure 2.2. When fuel, oxidizer and ignition source are present at necessary levels, burning will occur if the concentration of the mixture is within the flammability range. This means a fire will not occur if one of these three elements is missing; (1) fuel is not present or is not present in sufficient quantities, (2) an oxidizer is not present or is not present in sufficient quantities and (3) the ignition source is not energetic enough to initiate the fire.

In the past the sole method for controlling fires and explosions was elimination of or reduction in ignition sources (Crowl & Louvar, 2002). Practical experience has shown that this is not robust enough – the ignition energies for most flammable materials are too low and ignition sources too plentiful. As a result, current practice is to prevent fires and explosions by continuing to eliminate ignition sources while focusing efforts strongly on preventing flammable mixtures. An understanding of fire characteristics and behaviour of flammable materials both when contained and when released is necessary so that correct responses may be designed into a facility or planned action to be taken (Nolan, 1996).

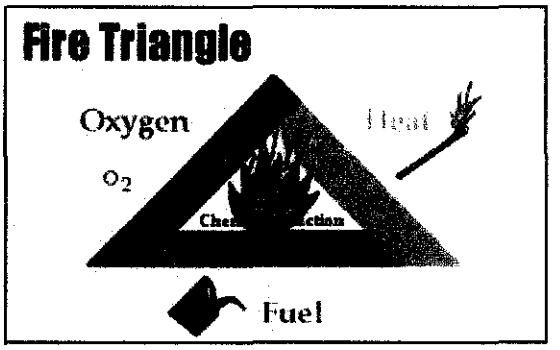

Figure 2.2: The fire triangle.

There are many organizations that have been developed classifications related to flammable chemicals, including Department of Transportation (DOT), National Fire Protection Association (NFPA), Occupational Safety and Health Administration

(OSHA), and Environmental Protection Agency (EPA). Some organizations establish their classifications with qualitative descriptions but most classifications are based on physical/chemical properties such as flash point and boiling point (Vázquez, 2005). Both NFPA and DOT defined combustible liquids as having a flash point of 100°F (38°C) or higher. On the other hand, OSHA defined combustible liquids as any liquid with a flash point at or above 100°F (38°C) but below 200°F (93.3°C) (Lee, 2005) NFPA have adopted the flash point as a criterion in enforcing the safe handling, storing, and transporting of flammable compounds (Fujii and Hermann, 1982).

2.2.1 Flammable mixture

A mixture of fuel-air will only burn if the fuel concentration is between the UFL and LFL. Figure 2.3 shows the flammable range for some fuel-air mixtures (Bjerketvedt et al., 1997).

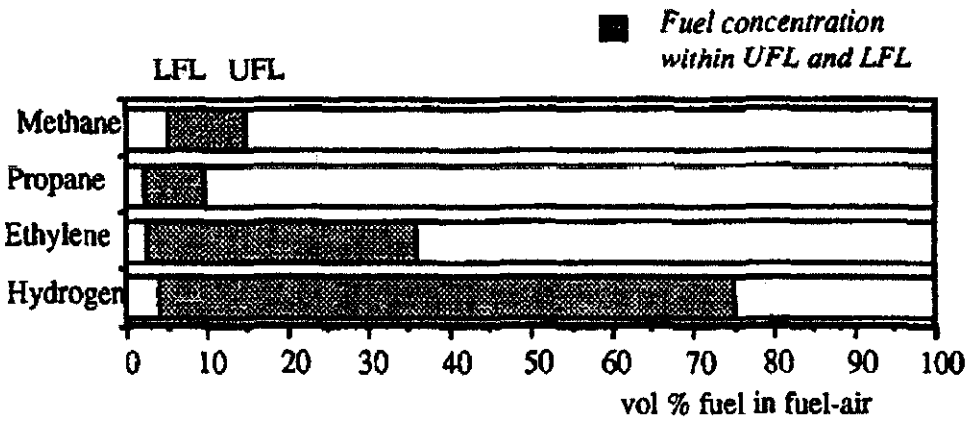

Figure 2.3: Flammability range for fuel-air mixtures at 1 atm. and 25°C.

The flammability in air is the most important safety characteristic of gases and gas mixtures (Volkmar and Maria, 2005). The flammability characteristics of chemical substances are important to prevent accidental explosions during industrial processes and handling flammable gasses. The gas mixture is classified as flammable if it is in between the explosion range. Thus, the explosion limits have to be

measured as it is interchangeable with the term flammability limit. The flammable mixture may form either by accident or design. The combustible concentration can be reduced by adding enough air or inert gas to produce non flammable mixtures when they are formed by accident. However, there are certain conditions to increase the combustible concentrations to produce a non flammable mixture. Flammable mixtures may encounter in production of many chemicals and physical operations. Thus, special precautions must be taken to assure no rapid formation of flammable mixture in the industry (Zabetakis, 1965). Flammable mixtures are composed of two or more flammable compounds. There will be different behaviours can be expected from the mixtures but it is depending whether the mixture is ideal or non-ideal (Vazquez, 2005).

In order to determine suitable hazard control measures, flammable and combustible liquids are classified according to their degree of hazard. Table 2.2 illustrates these classifications.

Table 2.2: Flammable and Combustible liquids

FLAMMABLE LIQUIDS		
A flammable liquid has a flashpoint below 100°F and a vapor pressure not exceeding 40 pounds/square inch (absolute) at 100°F		
CLASS IA	Flammable liquids with a flashpoint below 73°F and boiling point below 100°F.	Examples: Acetaldehyde, Ethylene Oxide, Ethyl Ether, Methyl Chloride.
CLASS IB	Flammable liquids with a flashpoint below 73°F and boiling point at or above 100°F.	Examples: Acetone, Hexane, Methanol, Gasoline, Toluene.
CLASS IC	Flammable liquids with a flashpoint at or above 73°F and below 100°F.	Examples: Butyl Acetate, Butyl Alcohol, Xylene, Propyl Alcohol.
COMBUSTIBLE LIQUIDS		
A combustible liquid has a flashpoint at or above 100°F.		

CLASS II	Combustible liquids with a flashpoint at or above 100°F and below 140°F.
CLASS IIIA	Combustible liquids with a flashpoint at or above 140°F and below 200°F.
CLASS IIIB	Combustible liquids with a flashpoint at or above 200°F.

Source: Flammable and Combustible Liquids Code, National Fire Protection Association, Quincy, MA. Note: 73°F = 22.8°C, 100°F = 37.7°C, 140° F = 60°C, 200°F = 93.33°C, 40 psi = 276 kilopascals.

Le Chatelier, (1891) proposed empirical models to calculate the LFL and UFL of multiple fuel mixtures. This method is still widely used today. Hustad and Sønju, (1988) found a good agreement between their experiments and Le Chatelier's law for LFL at elevated temperature and pressure for fuel mixtures. Thornton, (1917) developed a method to estimate the flammability limits from the oxygen coefficient for stoichiometric combustion. Jones, (1938) developed models to estimate LFL and UFL for hydrocarbon based on stoichiometric concentration. Jones noted for paraffin the LFL is close to 55% of the stoichiometric concentration, and similarly the UFL is about twice the stoichiometric concentration. Goto and Hirai, (1952) proposed a model to estimate the LFL based on heat of combustion. Spakowski, (1955) produced a model to estimate flammability limits based on the heat of combustion.

From previous works, there are also several researchers using another method to estimate the flammability characteristics of some chemicals which is experimental work using 20-L-explosion-apparatus. For example, Shu and Wen, (2002) conducted experiments to investigate the safety flammability limits, minimum oxygen concentration, maximum explosion overpressure, and flammability zone of o-xylene. Chang et al., (2007) used 20-L explosion vessel to study the flammability characteristics of the 3-picoline/water mixtures. Brooks and Crowl, (2007) utilized a 20-L combustion explosion apparatus to study the flammability of vapors above

aqueous solutions of ethanol and acetonitrile. In general, there are many differences between all these methods.

However, such experimental works are not really implemented nowadays because they are very costly and time consuming. Therefore, for some situations it may be necessary to estimate the flammability limits without experimental work instead using theoretical models that have been develop.

2.2.2 Flammability Limits of Liquid Solution

The biodiesel liquid sample will vaporize some components if it is exposed to some heat at higher temperature. Consequently, it is necessary to estimate the vapour compositions, which contribute to the flammable mixture. Affens and Mclaren, (1972) have derived equations to be used to estimate overall flammability properties of mixtures from the properties and proportions of the individual components. Melhem, (1997) presented a general method for estimating the flammability envelopes for chemical mixtures based on chemical equilibrium. Chang et al., (2005) studied the flammability characteristics of a binary solution for the mixture of benzene and methanol at various vapour-mixing ratios under 150°C temperature, 760 and 1,520 mmHg pressure by using a 20-L spherical explosion vessel. Brooks and Crowl, (2007) experimentally measured the LFL, LOC and the maximum safe solvent concentration (MSSC) for ethanol and acetonitrile above aqueous solutions.

Liquid mixtures can be divided into two categories: ideal solutions and non-ideal solutions. An ideal solution can be defined as a solution with thermodynamic properties similar to those of a mixture of ideal gases. The ideal solutions obey to the Raoult law. Furthermore, ideal solutions are solutions for which the activity coefficients are equal to 1 for all compounds. Whereas, for non-ideal solutions, the activity coefficient for at least one component in that solution is not equal to 1. (Catoire, and Paulmier, 2006).

2.2.2.1 Ideal Solution

In an ideal solution, both interactions between both chemicals are equal. These mixtures follow Raoult's law behaviour.

The activity coefficient for an ideal solution is 1. These solutions result from mixing two similar materials and no differential energies of interaction are encountered between the components. However, most solutions are not ideal.

2.2.2.2 Real Solution

It should be noted that Raoult's Law only works for ideal mixtures. Thermodynamically, the relation between an ideal vapour and a non-ideal liquid is represented by the equilibrium condition. A combination of Raoult's and Dalton's laws can be used to estimate the amount of vapour mixture formed about any hydrocarbon solution.

Non-ideal solutions have an activity coefficient value smaller or greater than 1. Real mixture is also known as non-ideal mixture. The mixture is positive deviations from Roult's law if more molecules than ideal mixtures will escapes to the vapour phase and raises the vapour pressure. Thus, a higher vapour pressure will results in a lower flash point value to reach LFL if both chemicals are flammable. However, the mixture is negative deviations from Roults law if the mixture vapour pressure is lower than the vapour pressure of the individual component. Therefore, mixture flash point values are expected to be higher than the pure component flash points (Vazquez, 2005).

2.2.3 Flammability Diagram

A general way to represent the flammability of a gas or vapor is by the triangle flammability diagram shown in Figure 2.4. Application of flammability diagram is the safest method to prevent fires and explosions of flammable mixtures in the first place (Mashuga and Crowl, 1998). The most useful tool to display the flammability

region, and to determine if a flammable mixture is present during plant operations is a triangular flammability diagram (Mashuga and Crowl, 2004). Each apex of the triangle represents 100% fuel, oxygen, and nitrogen. Concentration of fuel, oxygen and inert material (in volume or mole %) are plotted on the three axes. The shaded area represents the flammability zone which means any mixture lies in there are flammable. Those mixtures outside the flammability zone are considered non flammable and safe. In this study, the vapor mixture from bio fuels liquid lies under fuel category. All possible combinations of fuel plus air will represent as air line. Meanwhile, the stoichiometric line represents all stoichiometric combinations of fuel plus oxygen. In the diagram, the UFL and LFL are shown as the intersection of the flammability zone boundary with the air line. Any gas mixture containing oxygen below the LOC is not flammable. Flammability diagram is dependable with fuel type, temperature, pressure and inert species (Crowl and Louvar, 2002).

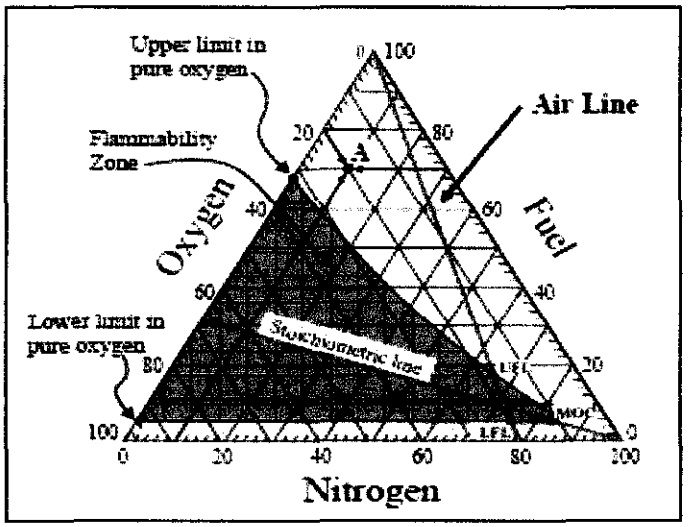

Figure 2.4: Flammability diagram.

2.3 Flammability Characteristics

The deep understanding on flammability characteristics can help in eliminating fire hazards when handling hazardous chemicals which are: lower flammability limit (LFL), upper flammability limit (UFL), limiting oxygen concentration (LOC), autoignition temperature (AIT), flash point (FP) and ignition sources.

There is not a single parameter that defines flammability, but some of the relevant properties are: flash point (FP), lower flammable limit (LFL), upper flammable limit (UFL), and autoignition temperature (AIT) (Vázquez, 2005). The relationship among these properties is presented in Figure 2.6 (Zabetakis, 1965).

LFL, and UFL is the lowest and highest concentrations (percentage) of a vapour in air capable of producing a flash of fire in presence of an ignition source. LOC is the limiting concentration of oxygen where below this limit combustion is not possible, independent of the concentration of fuel. It is also called as minimum oxygen concentration (MOC) and is expressed in units of volume percent of oxygen. AIT sometimes called the spontaneous ignition temperature (SIT) is the temperature at which the vapor ignites spontaneously from the energy of environment. The AIT is the minimum temperature required to cause self-sustained combustion (NFPA, 1994). FP is the lowest temperature at which it gives off enough vapor to form an ignitable mixture with air. The flash point criterion is used by regulatory authorities to rate the flammability hazards of chemicals (Vázquez, 2005). Ignition sources are numerous which it is impossible to identify and eliminate all of them.

The number of carbons in an organic component or hydrocarbon compound determines its burning characteristic. However, a simple rule of thumb can be used in determining using hydrocarbon formula, whether it is a flammable gas or liquid or semi solid or solid. The number of carbon atoms in a hydrocarbon molecule gives the molecule its vapour density which influences the vapour pressure and the colour of the flame. From these factors the approximate boiling point, flash point, vapour density and vapour pressure can be calculated. Thus, the kind of substance that is burning can be determined.

Table 2.3: Classification of flammability according to DOT (Vázquez, 2005)

Purpose	Flammability Definition	Classification
Transportation	Flammable liquid is any liquid with $T_f < 141$ °F (60.5 °C) Combustible liquid is any liquid with 141 °F (60.5 °C) $< T_f < 200$ °F (93.3 °C).	Class 3 flammable liquids are defined as liquids having a T_f of not more than 141 °F (60.5 °C) or any material in a liquid phase with a T_f at or above 100 °F (37.8 °C)

Table 2.4: Classification of flammability according to NFPA (Vázquez, 2005)

Purpose	Flammability Definition	Classification	Hazard Rating	Liquid Definition	Hazard Description
Fire-fighting and fire Protection	A liquid is classified as flammable if it has a T_f of 100°F or lower, when tested by closed cup methods. Combustible liquids are those with T_f higher than 100 °F (37.8 °C)			$T_f < 73$ °F (22.8 °C) ; $T_b < 100$ °F (37.8 °C)	Flammable Materials will rapidly vaporize at atmospheric pressure and normal temperatures, or are readily dispersed in air and which burn readily.
		IB, IC	3	$T_f < 73$ °F (22.8 °C); $T_b \geq 100$ °F (37.8 °C) 100 °F (37.8 °C) > $T_f \geq 73$ °F (22.8 °C)	Flammable Liquids and solids can ignite under almost all temperature conditions.
				140 °F (60 °C) > $T_f \geq 100$ °F (37.8 °C)	Combustible Materials must be moderately heated or exposed to relatively high ambient temperatures before they will ignite.
				200 °F (93.3 °C) $\leq T_f \geq 140$ °F (60 °C)	
		IIIB	1	$T_f > 200$ °F (93.3 °C)	Combustible Materials must be preheated before they will ignite

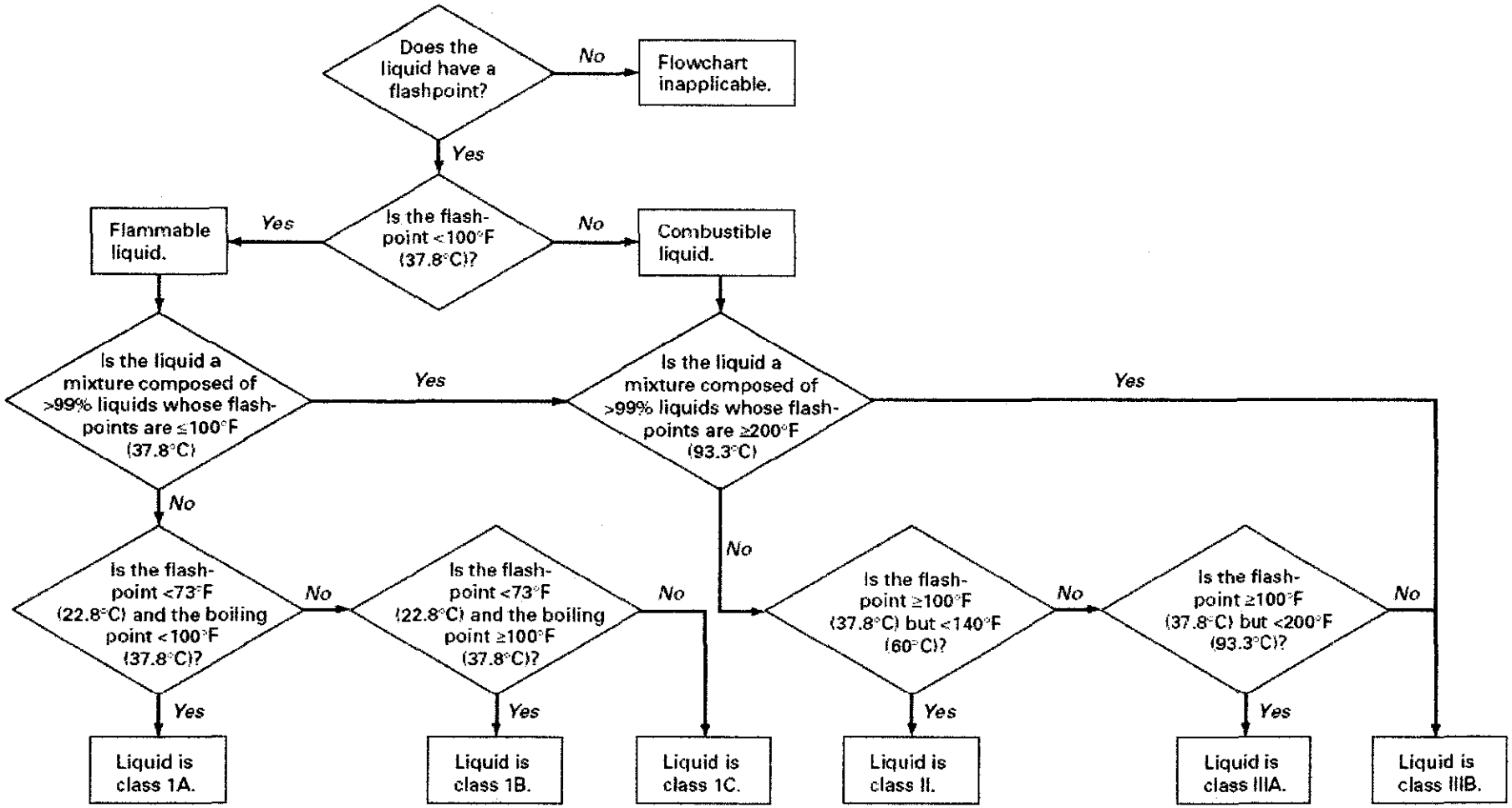

Figure 2.5: OSHA/NFPA classes of flammable and combustible liquids (Meyer, 2005).

Table 2.5: Comparison between standardised methods for the determination of the auto-ignition temperature (Norman, 2008)

method	EN 14522	DIN 51 794	IEC 60079-4	BS 4056-66	ASTM D2155-66	ASTM E 659-78	ASTM D2883-95
scope	$p = 1$ atm $T \leq 923$ K gases/vapours	$p = 1$ atm $T \leq 923$ K gases/vapours	$p = 1$ atm gases/vapours	$p = 1$ atm $T \leq 923$ K gases/vapours	$p = 1$ atm liquids	$p = 1$ atm liquids	$p \leq 0.8$ MPa $T \leq 923$ K liquids/solids
test vessel	borosilicate erlenmeyer $V = 200$ ml open	borosilicate erlenmeyer $V = 200$ ml open	borosilicate/quartz/ metal erlenmeyer $V = 200$ ml open	borosilicate/quartz/ metal erlenmeyer $V = 200$ ml open	borosilicate erlenmeyer $V = 200$ ml open	borosilicate round bottomed $V = 500$ ml open	steel explosion vessel $V = 1$ l closed
auto-ignition criterion	visual flame	visual flame	visual flame	visual flame	visual flame	visual flame	temp./press. recordings
time criterion	$t \leq 5$ min	$t \leq 5$ min	$t \leq 5$ min	$t \leq 5$ min	$t \leq 5$ min	$t \leq 10$ min	$t \leq 10$ min

EN 14522. Determination of the minimum ignition temperature of gases and vapors. British-Adopted European Standard.

DIN 51 794. Testing of mineral oil hydrocarbons - Determination of ignition temperature. DIN: Deutsches Institut Fur Normung E.V.

IEC 60079-4. Electrical apparatus for explosive gas atmospheres – Part 4: Method of test for ignition temperature. International Electrotechnical Commission.

BS 4056-66. Method of Test for Ignition Temperature of Gases and Vapours. British Standard Institution.

ASTM D2155-66. Method of Test for Autoignition Temperature of Liquid Petroleum Products. American Society for Testing and Materials.

ASTM E659-78. Autoignition temperature of liquid chemicals. American Society for Testing and Materials.

ASTM D2883-95. Standard Test Method for Reaction Threshold Temperature of Liquid and Solid Materials. American Society for Testing and Materials.

2.3.1 Flammability Limits

A combustible gas-air mixture can be burned over a wide range of concentrations-when either subjected to temperatures or ignition source (Zabetakis, 1965). Most hydrocarbons are extremely volatile under relatively normal operation conditions. A detailed knowledge of the flammability is needed to prevent workplace explosions of such flammable vapours (Zhao, 2008). Flammable limit values are often provided with material safety datasheets. According to ASTM (American Society for Testing and Materials), flammability limit can be defined as the maximum or minimum concentration of a combustible substance that is capable of propagating flame in a homogenous mixture of the combustible and a gaseous oxidizer under specified conditions of test (Rowley, 2010). Flammability limits are divided into two types: the upper flammable limit (UFL) and the lower flammability limit (LFL).

UFL can be defined as maximum fuel concentration to burn which is deficient in oxygen. Meanwhile, LFL is minimum fuel concentration where is too lean or sufficient in oxygen to be ignited (Zhao, 2008). A mixture is flammable when the composition is between the LFL and UFL and vapour air mixture will only ignite and burn in the specific range of composition.

LFL and UFL data for pure hydrocarbons are available in different literatures. However, hydrocarbon mixtures with different components and different mole fraction are often presented in the industry as having significant contributions to fire and explosion accidents. For some situations, it may be necessary to estimate the flammability limits without experimental data which not available in the literatures. Jones found that for many hydrocarbon vapors the LFL and UFL are a function of the stoichiometric concentration, C_{st} of fuel (Jones, 1938). Vapour-air mixtures ignite and burn only over a well-specified range of compositions. The mixture will not burn when the composition is lower than the lower LFL; that is the mixture is too lean for combustion. The mixture is also not combustible when the composition is too rich; that is, when it is above the UFL. A mixture is flammable only when the composition is between the LFL and the UFL (Crowl and Louvar, 2002).

Zabetakis and Richmond, (1953) suggested models Eq. (2-1) and Eq. (2-2) to obtain the flammability limits by determining the limiting mixture compositions between flammable and non flammable mixtures.

$$LFL_{,T,P} = \frac{1}{2}\left(C_{gn} + C_{lf}\right) \tag{2-1}$$

$$UFL_{,T,P} = \frac{1}{2}\left(C_{gf} + C_{ln}\right) \tag{2-2}$$

where,

$LFL_{,T,P}$ is the lower flammability limit at specific temperature and pressure,

$UFL_{,T,P}$ is the upper flammability limits at specific temperature and pressure,

C_{gn} is the greatest concentration of fuel in oxidant that are non flammable,

C_{lf} is the least concentration of fuel in oxidant that are non flammable,

C_{gf} is the greatest concentration of fuel in oxidant that are flammable, and

C_{ln} is the least concentration of fuel in oxidant that are flammable.

Liao et al., (2005) conducted an experimental to study the flammable limit of natural gas-air mixture to obtain the fundamental flammability data for prevention of the hazards in the practical applications. Kondo et al., (2007) completed a study on flammability limits of fuel mixture that introduce a modified Le Chatelier's formula to provide better interpret the flammability limits of fuel blends.

The rate at which a flame propagates through a flammable mixture depends on a number of factors including temperature, pressure, and mixture composition. It is a minimum at the limits of flammability and a maximum at near stoichiometric mixtures (Lewis, 1961; Zabetakis, 1965).

2.3.1.1 Flammability Limit Dependence on Temperature

When a flammable mixture is heated to an elevated temperature a reaction is initiated that may proceed with sufficient rapidity to ignite the mixture. The time elapses between the instant the mixture temperature raised and that in which a flame appears is called the time lag or time delay before ignition. In general, this time delay decreases as the temperature increases (Zabetakis, 1965). Burgess and Wheeler,

(1911) indicated that the heat liberated by a mole of flammable substance at the lean limit is nearly constant for a number of combustible-air mixtures at ambient temperature. Zabetakis et al., (1958) extended Burgess and Wheeler law to include the effect of initial temperature on the explosion limits. The resulting expression is a linear relationship between the lower explosion limit and the initial mixture temperature as indicated in Eq. (2-3) (Schoor and Verplaetsen, 2006):

$$\frac{LFL(T)}{LFL(T_0)} = 1 - c(T - T_0) \tag{2-3}$$

where,

T is the initial temperature,

T_0 the reference temperature (20 °C), and

c is a constant to be determined from the least squares fit.

Zabetakis, (1965) indicated that as the temperature is increased, the LFL decreases and the UFL increase. Flammable mixtures considered in Figure 6 fall in one of three regions. The first is left of the saturated vapour-air mixtures curve, in the region labelled "Mist". The second lies along the curve for saturated vapour-air mixtures; the last and most common region lies to the right of this curve. Compositions in the second and third regions make up the saturated and unsaturated flammable mixtures of a combustible-oxidant system at a specified pressure. Figure 6 shows that as the temperature increases, the range of flammability limits widens. Therefore, at room temperature a mixture which is not flammable can become flammable if temperature increases (Arnaldos et al., 2001). Zabetakis et al., (1959) reported that the flammability range increases with temperature. The following empirically derived equations Eq. (2-4) and Eq. (2-5) are available for vapours:

$$LFL_T = LFL_{25} - \frac{0.75}{\Delta H_c}(T - 25) \tag{2-4}$$

$$UFL_T = UFL_{25} + \frac{0.75}{\Delta H_c}(T - 25) \tag{2-5}$$

where,

ΔH_c is the net heat of combustion (kcal/mol),

T is the temperature (^{0}C), and

LFL and UFL in volume %.

Zabetakis, (1965) shows in Figure 2.7 the effect of temperature on LFL of 10 paraffin hydrocarbons in air at atmospheric pressure. Recently Kondo et al., (2011) measured the flammability limits for several combustible gases (methane, propane, isobutane, ethylene, propylene, dimethyl ether, methyl formate, 1,1-difluoroethane, ammonia, and carbon monoxide) at temperatures varying from 5 to 100 °C in a 12-L spherical flask basically following ASHRAE method. The results indicated that as the temperature rises, the LFLs are gradually decreasing and the UFLs are increasing.

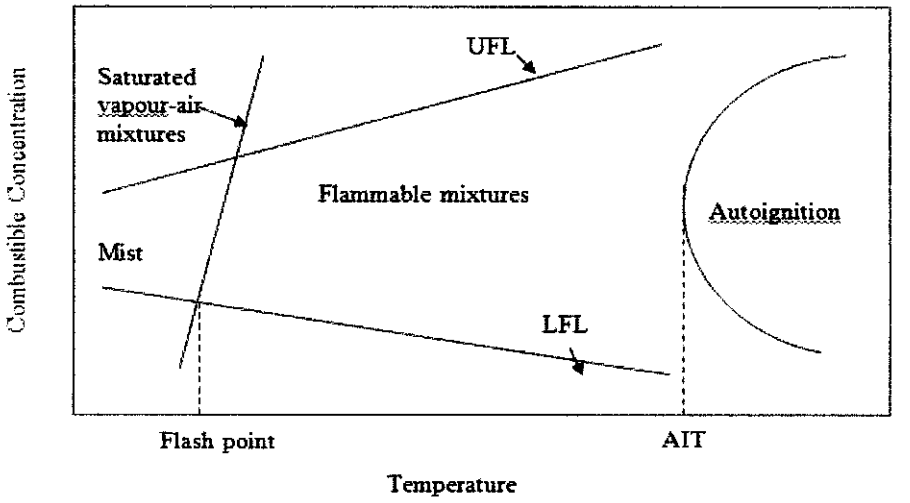

Figure 2.6: Effects of temperature on flammability limits (Zabetakis, 1965).

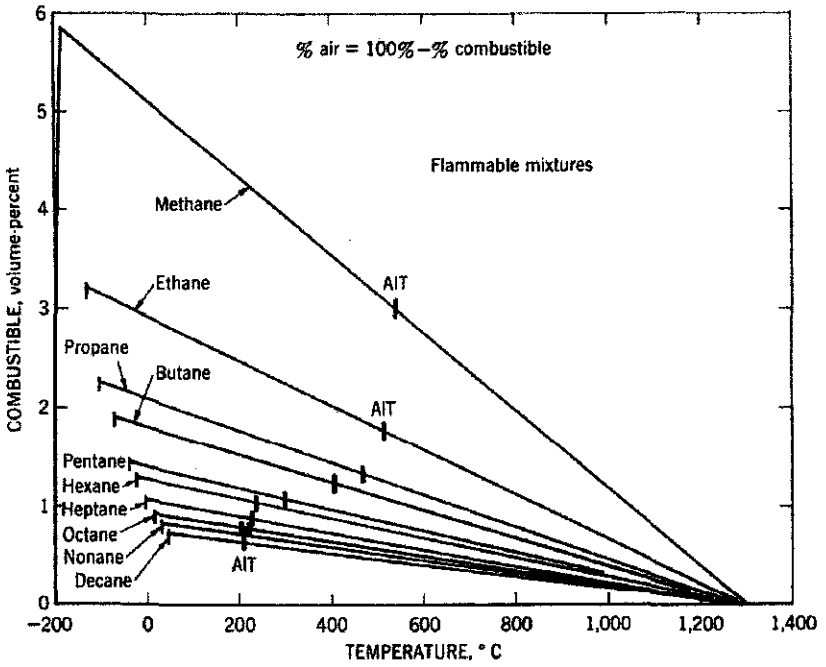

Figure 2.7: Effect of temperature on lower limits of flammability of 10 paraffin hydrocarbons in air at atmospheric pressure.

2.3.1.2 Flammability Limit Dependence on Pressure

Flammability limits also dependence on pressure except at very low pressure. LFL has small impact of system pressure while its impact on the UFL. As the pressure increased, the UFL will significantly increases and broadening the flammability range (Crowl and Louvar, 2002). Zabetakis, (1965) indicated that although the limits of flammability are not affected significantly by moderate changes in pressure, the temperature limits are pressure dependent. Jones et al., (1949) and Hanna et al., (1965) shown in Figure 2.8 the initial pressure effect of the flammability limits of natural gas.

Eq. (2-6) and Eq. (2-7) show empirical expressions for UFL as a function of pressure (Zabetakis, 1965):

$$LFL = 4.9 - 0.71 \log P \tag{2-6}$$

$$UFL = 14.1 + 20.4 \log P \tag{2-7}$$

where,

P is the initial system pressure in atmospheres, and

LFL, and *UFL* are the lower and upper flammable limits in volume %.

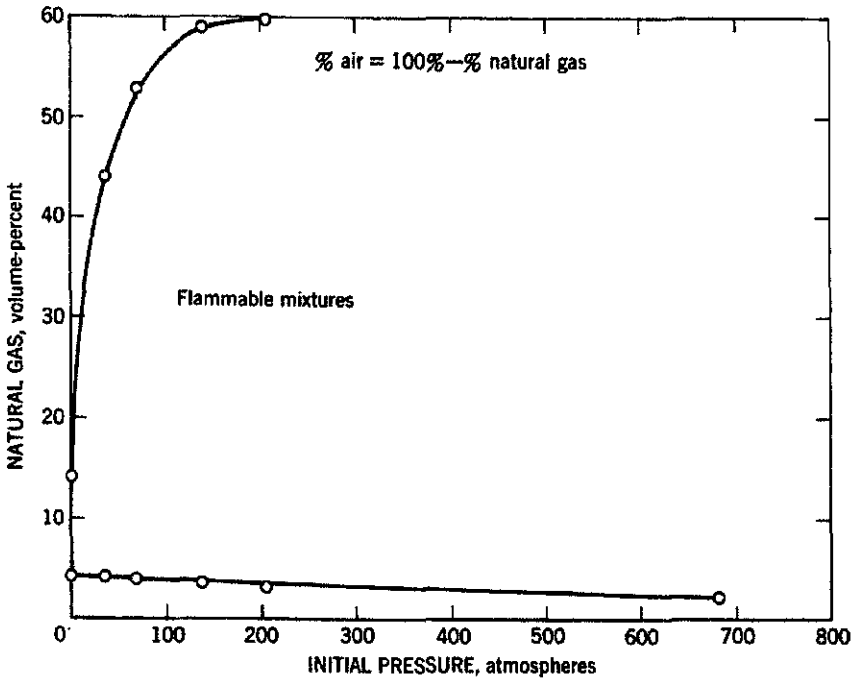

Figure 2.8: Effect of pressure on limits of flammability of natural gas in air at 280°C.

2.3.1.3 Composition Effects

Liquid hydrocarbon compositions can be confirmed by a comprehensive gas chromatography (GC). Several techniques such as gas chromatography–isotope ratio mass spectrometry (GC–IRMS) and Gas chromatography-mass spectrometry (GC-MS) are currently utilized by many researchers in different fields, such as fire and explosive investigations, environmental analysis and environmental chemistry. However, their potential to be used in the instigation of ignitable liquids is clear (Semenov, 1959). The use of GC-MS is to separate the mixtures of chemicals into its individual components. Generally, substances are identified (qualitatively) by the order in which they emerged (elute) from the column and by their retention time in the column. It should be noted that the analysis of sample compositions is not enough to predict whether the mixture is considered flammable or not. In this regard, material's ignition resistance is a critical measure of flammability since if there is no

fire hazard, ignition does not occur. Although under some circumstances prolonged non-flaming gasification or smoldering may represent a threat to life safety (Lautenberger et al., 2006).

It can be noted from Zabetakis and Richmond, (1953) models, Eq. (2-1) and Eq. (2-2) that the flammability limits are calculated based on mixture compositions. Zabetakis, (1965) indicated that flame propagates through a flammable mixture depends on a number of factors including temperature, pressure, and mixture composition.

2.3.2 Limiting Oxygen Concentration (LOC)

Limiting oxygen concentration (LOC) is the minimum oxygen concentration required to propagate a flame (Crowl and Louvar, 2002). Fire and explosion can be prevented by reducing the concentration of oxygen. Vapour mixture cannot generate the reaction enough energy if below LOC. LOC can be measured using flammability apparatus (Coward and Jones, 1952; Zabetakis et al., 1965; Kuchta, 1985). ASTM also developed a standard test method E2079 to estimate the LOC of mixtures of oxygen and inert gases with flammable gases and vapors at a specified initial pressure and initial temperature (ASTM E2079-07).

However, in absence of experimental work, LOC value is estimated using stoichiometry of the combustion reaction of hydrocarbon (Crowl and Louvar, 2002). LOC work can be found in different literature. Domnina et al., (2003) also has described a new algorithm to estimate the LOC by using the values of lower explosion limit (LEL) of the fuel mixture and the calculated adiabatic flame temperature (CAFT). Isaac and Gregory (2009) presents data on the limiting (minimum) oxygen concentration (LOC), in the presence of added N_2, of methane (CH_4), propane (C_3H_8), ethylene (C_2H_4), carbon monoxide (CO), and hydrogen (H_2), and some of their binary mixtures. If experimental and literature data are not available, the LOC is estimated by using the stoichiometry from the combustion reaction and the LEL. This procedure works quite well for many different hydrocarbons (Siwek, 1996; Crowl and Louvar, 2002).

LOC can be estimated using the stoichiometry of the combustion reaction and the LFL. Eq. (2-8) can be used to estimate LOC (Crowl and Louvar, 2002):

$$LOC = \left(\frac{moles\ of\ fuel}{total\ moles}\right)\left(\frac{moles\ of\ O_2}{moles\ fuel}\right) = LFL\left(\frac{moles\ of\ O_2}{moles\ fuel}\right) = z(LFL) \quad (2\text{-}8)$$

LOC for a mixture can be also estimated using a method of Zlochower and Green, 2009).

Hansen and Crowl developed a better equation to estimate LOC (Eq. (2-9)) (Hansen & Crowl, (June 2010)).

$$LOC = \left(\frac{LFL - C_{LOC}UFL}{1 - C_{LOC}}\right)\left(\frac{UFL_0}{UFL}\right) \quad (2\text{-}9)$$

where,

LOC is the limiting oxygen concentration for the vapor mixture (percent oxygen),

UFL is the upper flammability limit (percent fuel in air),

LFL is the lower flammability limit (percent fuel in air),

UFL_0 is the oxygen concentration at the upper flammability limit (vol% oxygen in air), and

C_{LOC} is a fitting constant = -1.11.

2.4 Inherent Safer Design

Inherent safer design is design that avoids hazards instead of controlling them, particularly by reducing the amount of hazardous material and number of hazardous operation in the plant. The concept of reducing rather than controlling hazards comes from Kletz, (1978). An inherent safe plant relies on chemistry and physics to prevent accidents rather than on control systems, interlocks, redundancy, and special operating procedures (Crowl and Louvar, 2002). An inherently safe process has a low level of danger even if things go wrong. Inherent safer plants are tolerant of errors and are often most cost effective. There are four inherent safety techniques

which are minimize (intensification), substitute (substitution), moderate (attenuation and limitation of effects) and simplify (simplification and error tolerance). Now, this concept is widely applied in pursuing the reduction of the hazards in industrial processes. Inherent safety is a design approach useful to remove or reduce hazards at the source instead of controlling them with add-on protective barriers (Vázquez, 2005). Inherent safety, also called primary prevention, consists in the elimination of a hazard (Hansson, 2010). In industry, there is no chemical process that is without risk, but all chemical process can be made safer (Bollinger et al., 1996). A good practice in inherent safety is instead of controlling the hazards; the hazards are avoided by reducing the amount of hazardous material and number of hazardous operation in the plant.

CHAPTER 3

METHODOLOGY

3.1 Introduction

The methodology of this project was developing a systematic way to examine if the vapor mixture of biodiesel from production processes and storage systems is flammable or not. This vapor mixture is formed by vaporization of biodiesel components when being exposed to certain range of temperatures at atmospheric pressure. The values of flammability characteristics such as LFL, UFL and LOC can be measured using experimental apparatus, which can be costly and time consuming. However, there are several components do not have their values. Therefore, it is convenient to estimate these values theoretically using empirical equations. The methodology of this work was divided into two parts. The first part will be the experimental works where the biodiesel being produced and analyzed using Headspace Gas Chromatography Mass Spectroscopy (GC-MS) to examine the vapor mixture forms when biodiesel being exposed to different range of temperatures. This vapor mixture is formed by vaporization of organic components contained in the biodiesel. The second part of this work was covered the theoretical methods used in estimating the flammability characteristic of biodiesel vapor mixture. Simulation software such as COSMO and ThermoSolver were used to calculate the activity and fugacity of each component exist in biodiesel vapor mixture.

Figure 3.1 shows the methodology of this project integrates experimental, simulation and theoretical assessments.

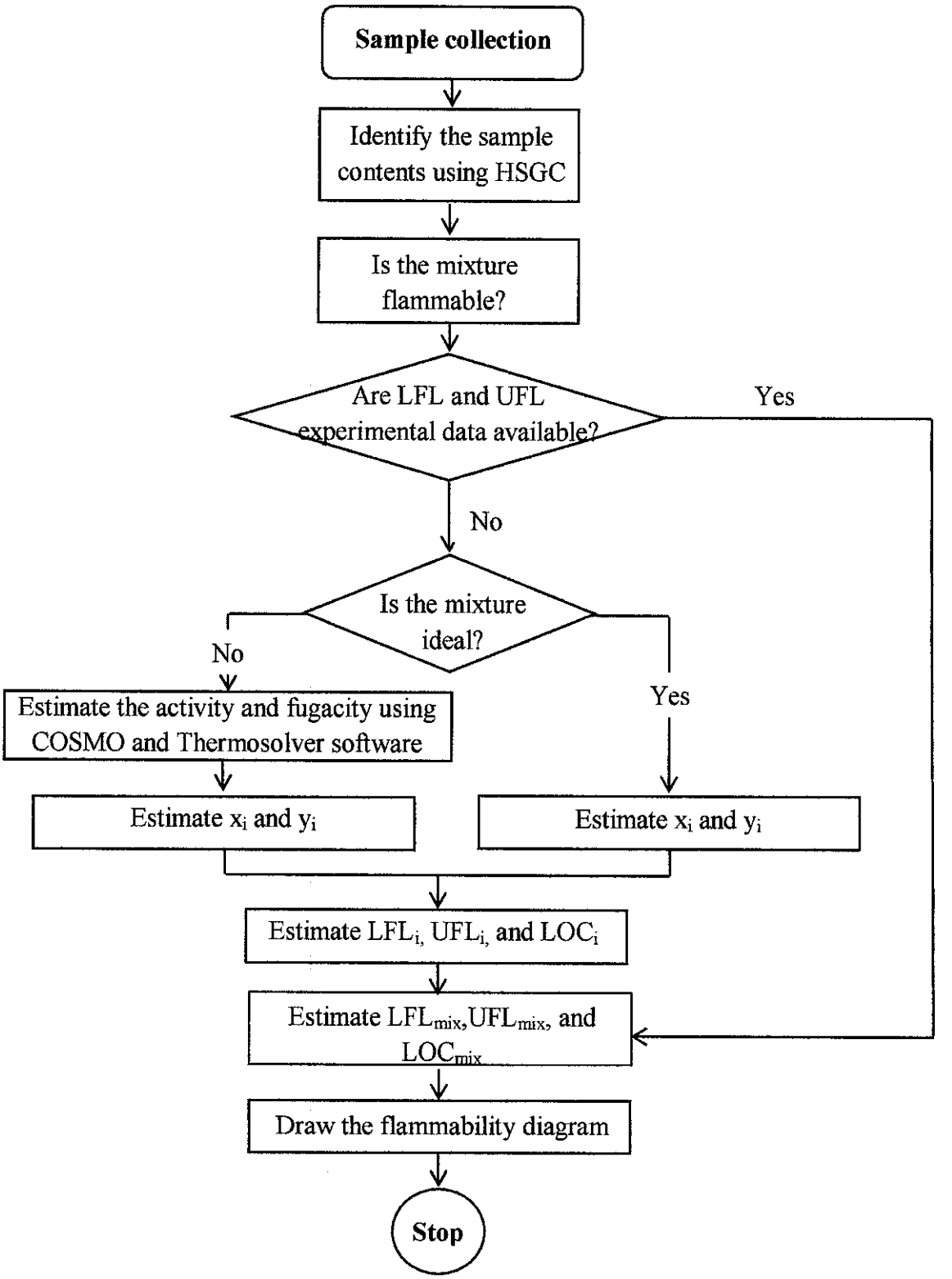

Figure 3.1: Flowcharts describe the methodology steps.

3.2 Experimental and Theoretical Works

3.2.1 Biodiesel production

For this study, biodiesel is produced by transesterification process where it involves the reaction between vegetable oils, and a short-chain aliphatic alcohols which is methanol using potassium hydroxide as catalyst. This process is two step reactions and takes place at 40°C. Figure 3.2 shown vegetables oil and methanol being heated and stirred for about 2 hours where biodiesel and glycerol is produced as final product. After the reactions have been completed, biodiesel and glycerol is separated by settling process as shown in Figure 3.3. After first settling process, the biodiesel is separated from glycerol and is weighed. Then, biodiesel is mixed with a certain amount of water in the settling bottle. That bottle is then shaken and left to settle for an hour. This settling process is repeated three times. Then the biodiesel product is dried using anhydrous sodium sulfate as drying agent to remove all the water to get the purified biodiesel liquid sample. This purified biodiesel sample is used in experimental work to analyze the composition of biodiesel liquid sample by injecting biodiesel vapor mixture at various temperatures into GC-MS. Data retrieved from GC-MS is used in the theoretical work to identify the flammability of biodiesel.

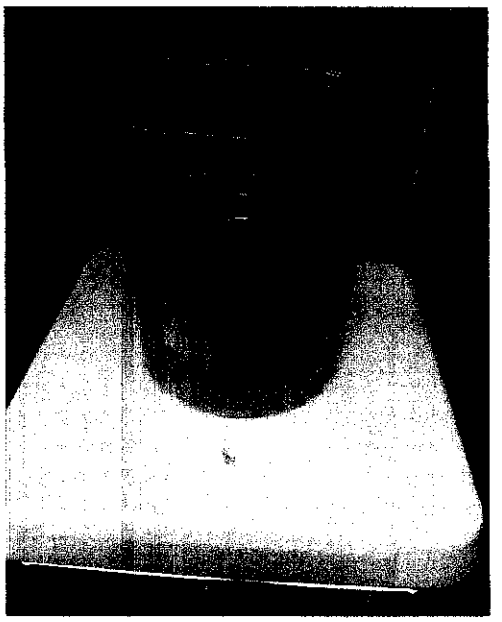

Figure 3.2: production of biodiesel from vegetables oil and methanol.

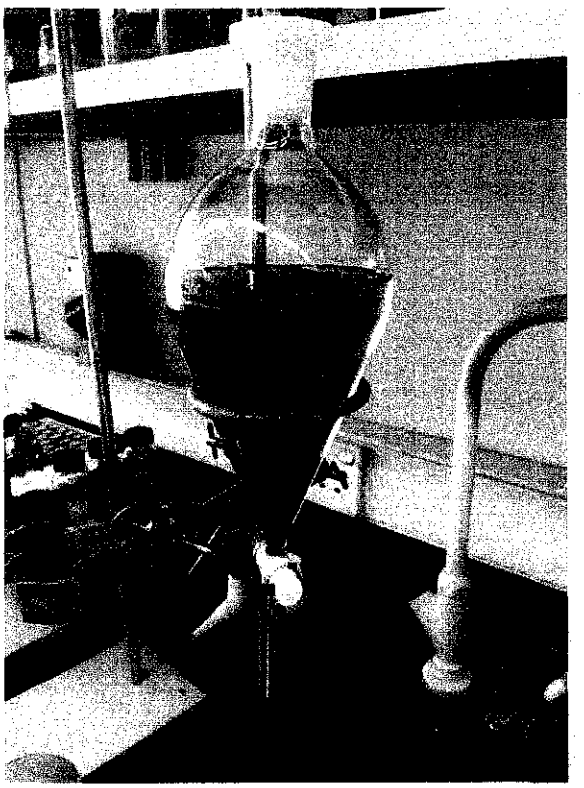

Figure 3.3: Settling process.

3.2.2 Composition

The composition of the biodiesel was analyzed using Gas Chromatography (GC) at different range of temperature; 50°C, 100°C, 150°C and 200°C. The vapor mixtures vaporized from biodiesel sample were injected into Gas Chromatography Mass Spectrometry (GC-MS). GC-MS was performed with Agilent Technology 7890A column and MS detector, using 30x250x0.25 mm capillary column using the following settings: Electron impact ionization, electron energy 70 eV and scan range 40 - 500 amu at 1 scan/s. The carrier gas (Helium 99.999%) flow rate was set to 1.5 ml/min with column inlet pressure 54.8 kPa and linear velocity 36.10 cm/sec. Sample was injected into a HP5 fused silica (5% phenyl polysilphenylene-siloxane) capillary column BPX5 (30 m length; 0.25 mm i.d.; 0.25 μmfilm thickness). GC-MS was used to identify the compounds in the evaporated fraction of the liquid. GC-MS identifies different compounds at different times (retention times) depending on their chemical structures and the result shown peak areas and retention time. The peaks obtained from GC-MS spectrum was compared with all the components peaks in the GC-MS

library to find the most accurate match for each component exist in biodiesel vapor mixture.

3.2.2.1 Mole Fraction in Liquid Phase

The mass fraction of each component in biodiesel sample can be calculated using GC data. From GC data and chromatogram, the mass fractions of each component exist in biodiesel is calculated based on peak area of individual components and the total peak area using Eq. (3-1):

$$\chi_i = \frac{A_i}{A_T} \tag{3-1}$$

where,

χ_i is the mass fraction of component i,

A_i is the peak of area of component i, and

A_T is the peak of all components.

Then the mass fraction is converted to mole fraction using Eq. (3-2):

$$x_i = \frac{\chi_i / M_i}{\sum \chi_i / M_i} \tag{3-2}$$

where,

x_i is the mole fraction of component i in the liquid phase, and

M_i is the molecular weight of component i.

3.2.2.2 Mole Fraction in Vapor Phase

In order to estimate the flammability of biodiesel vapor mixtures, the mole fraction in vapor phase is calculated. To calculate the mole fraction in vapor phase, the liquid solution should be first identified whether it is ideal or non ideal solution.

Ideal Solution

In an ideal solution, the two species in the mixture are almost identical chemically. These mixtures follow Raoult's Law, in which the equilibrium condition between the liquid and vapor phase is represented by Eq. (3-3):

$$x_i P_i^{sat} = y_i P_T \tag{3-3}$$

where,

x_i is the mole fraction of component i in the liquid phase,

P_i^{sat} is the vapor pressure of component i as a pure component,

y_i is the mole fraction of component i in the vapor phase, and

P_T is the total pressure.

Non Ideal/Real Solution

Raoult's Law can be modified to non ideal solutions by incorporating two factors that will relate the interactions between molecules of different substances which are; fugacity coefficient (φ_i) and activity coefficient (γ_i).

The modified Raoult's Law is used to calculate the mole fraction in the vapor phase for each component.

$$\gamma_i x_i P_i^{sat} = \varphi_i y_i P_T \tag{3-4}$$

where,

γ_i is the activity coefficient for component i,

x_i is the mole fraction of component i in liquid phase,

P_i^{sat} is the vapor pressure of component i as a pure component,

φ_i is the fugacity coefficient for component i, and

y_i is the mole fraction of component i in the vapor phase.

Since in this study, the mixture is considered as real solution, the fugacity and activity coefficients for each component are calculated using established methods. COSMO software was used to estimate the activity coefficients while Thermosolver software based on Peng-Robinson method was used to calculate the fugacity coefficients at different range of temperatures.

The vapor pressures of the components were calculated according to the Antoine equation as in Eq. (3-5).

$$\log_{10} P^{sat} = A - \frac{B}{C+T} \tag{3-5}$$

Where A, B and C are the component-specific constants. These constants were collected from Yaws' Handbook of Antoine Coefficients for Vapor Pressure (2010) and valid for certain range of temperatures between T_{min} and T_{max}.

3.2.3 LFL and UFL for Individual Components

Flammability limits have been determined without using experimental data. It should be noted that the LFL and UFL will be calculated in the vapour phase. Jones (1938), found that for many hydrocarbon vapours, the LFL and UFL are functions of the stoichiometric concentration of fuel (C_{st}) Eq. (3-6) and Eq. (3-7):

$$LFL = 0.55C_{st} \tag{3-6}$$

$$UFL = 3.5C_{st} \tag{3-7}$$

where,

C_{st} is the volume % fuel in fuel plus air.

Using the general combustion reaction Eq. (3-8), the stoichiometric concentration for most organic compound can be determined.

$$C_m H_x O_y + zO_2 \rightarrow mCO_2 + \left(\frac{x}{2}\right) H_2O \tag{3-8}$$

where z is equivalent to moles O_2/moles fuel and can be found from Eq. (3-9):

$$z = m + \frac{x}{4} - \frac{y}{2} \tag{3-9}$$

The stoichiometric concentration (C_{st}) is determining using Eq. (3-10):

$$C_{st} = [\text{moles fuel}/ (\text{moles fuel} + \text{moles air})] \times 100$$

$$= \frac{100}{[1 + (z/0.21)]} \tag{3-10}$$

Substituting z and applying Eq. (3-6) and Eq. (3-7) yields

$$LFL = \frac{0.55(100)}{4.76m + 1.19x - 2.38y + 1} \tag{3-11}$$

$$UFL = \frac{3.50(100)}{4.76m + 1.19x - 2.38y + 1} \tag{3-12}$$

For flammability limits dependence on temperature, LFL and UFL are calculated using the following empirically derived equations available for vapors as in Eq. (3-13) and Eq. (3-14):

$$LFL_T = LFL_{25} - \frac{0.75}{\Delta H_c}(T - 25) \tag{3-13}$$

$$UFL_T = UFL_{25} + \frac{0.75}{\Delta H_c}(T - 25) \tag{3-14}$$

where,

ΔH_c is the net heat of combustion (kcal/mole) and

T is the temperature (°C)

3.2.4 LFL and UFL for Vapor Mixture

The LFL and UFL for the mixture are calculated using the Le Chatelier equation as in Eq. (3-15) and Eq. (3-16):

$$LFL_{mix} = \frac{1}{\sum (y_i / LFL_i)} \tag{3-15}$$

$$UFL_{mix} = \frac{1}{\sum (y_i / UFL_i)} \tag{3-16}$$

where,

LFL_i, is the lower flammable limit for component i (in volume %) of component i in fuel and air,

UFL_i, is the upper flammable limit for component i (in volume %) of component i in fuel and air

$y_i$is the mole fraction of component i on a combustible basis and

3.2.5 Limiting Oxygen Concentration (LOC) for Vapor Mixture

Hansen and Crowl (2010) developed a better equation to estimate the LOC (Eq. 3-17))

$$LOC = \left(\frac{LFL - C_{LOC} UFL}{1 - C_{LOC}} \right) \left(\frac{UFL_o}{UFL} \right) \tag{3-17}$$

where,

LOC is the limiting oxygen concentration for the vapor mixture (percent oxygen),

UFL is the upper flammability limit (percent fuel in air),

LFL is the lower flammability limit (percent fuel in air)

UFL_o is the oxygen concentration at the upper flammability limit (vol% oxygen in air), and

C_{LOC} is a fitting constant = -1.11

3.3 Constructing the Flammability Diagram

A general way to represent the flammability of a vapor is by the triangle diagram consist of three axes. On these axes, the concentration of fuel (vapor mixture from vaporization of bio oil), oxygen, and inert material (in volume or mole %) are plotted for this study. The value of LFL_{mix}, UFL_{mix}, and LOC_{mix} found in this study have been used to construct flammability diagram. From this flammability diagram, the flammability of vapor mixture from biodiesel liquid sample at different range of storage temperature varies from 25°C to 50°C and atmospheric pressure have been identified. To approximate the flammability zone, three methods have been developed; described in detail by Crowl and Louvar (2002).

3.4 Tool and Equipment

- Gas Chromatography Mass Spectrometry (GC-MS)
- COSMO software
- Thermosolver Software based on Peng-Robinson method
- Microsoft Office Excel

3.5 Key Milestone & Gantt Chart

1	Project Work Continues								mid-semester break								
2	Submission of Progress Report									●							
3	Project Work Continues																
4	Pre-EDX												●				
5	Submission of Draft Report													●			
6	Submission of Dissertation (soft bound)														●		
7	Submission of Technical Paper														●		
8	Oral Presentation															●	
9	Submission of Project Dissertation (hard bound)																●

Figure 3.4: Key milestone and gantt chart of FYP.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Introduction

This chapter discusses the method that should be applied when evaluating the flammability of a vapor mixture and examine if the existing vapor mixture is flammable or not. As elaborated in chapter three, the LFL, UFL and LOC are predicted using theoretical methods. These values will be used to construct the flammability diagram at different temperature to investigate the flammability of biodiesel vapor mixture. Moreover hazards classification will be studied based on the components presented in the biodiesel sample at different range of temperature. Finally the results from this study will be integrated together and inherent safety recommendation will be introduced and discussed to help in preventing fire accidents due to accumulating of flammable vapors from biodiesel.

4.2 Composition

Total components exist in biodiesel are different at different temperatures. Since biodiesel has higher boiling point which is about 330°C-357°C, more components will vaporized only at higher temperature. When biodiesel is heated at 50°C and 100°C, there is no component detected by GC-MS. Figure 4.1 and Figure 4.2 show the retention time and peak appear for biodiesel vapor mixture at 50°C and 100°C from GC-MS. These figures indicated that no components exist at the above temperatures. It can be concluded that there are no components vaporized from biodiesel at lower temperature; 50°C and 100°C therefore, biodiesel is not flammable. At higher temperature; 150°C and 200°C, several peaks appear in GC-MS data including unnecessary peaks indicated some components have vaporized from biodiesel liquid sample at those temperatures. The unnecessary peak refers to the peak with no exact component representing it and it will not affect the

composition of biodiesel vapor mixture. The unnecessary peaks will not contribute in the theoretical calculation to investigate the flammability of biodiesel at these temperatures. The components detected by GC-MS at 150°C ranging from C_9 to C_{17} while at 200°C the components ranging from C_9 to C_{19}. It can be concluded that as temperatures increased, components with longer carbon chains will vaporized. Figure 4.3 and Figure 4.4 show the retention time and peaks appear when biodiesel vapor mixture is vaporize at 150°C and 200°C respectively.

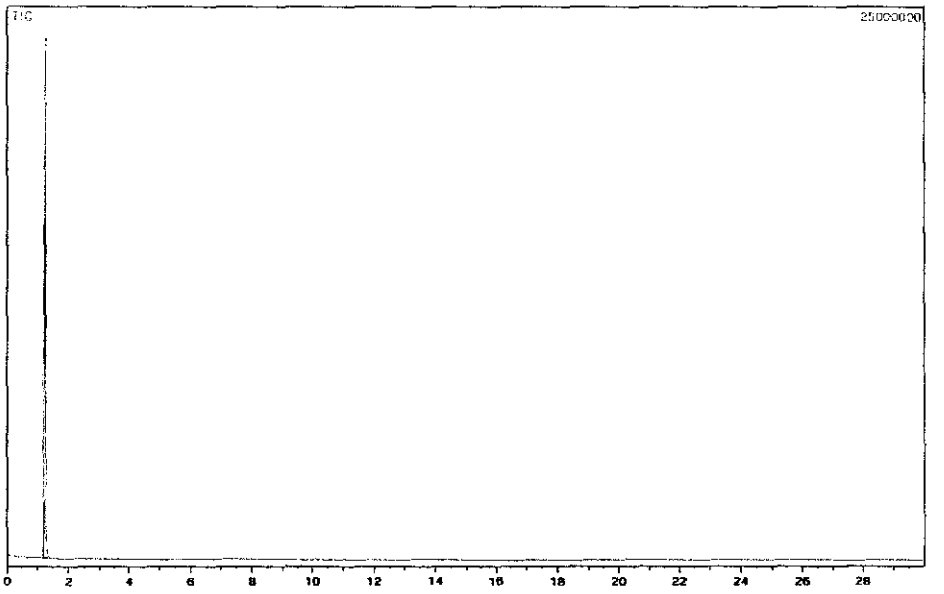

Figure 4.1: GC-MS analysis for biodiesel sample at 50°C.

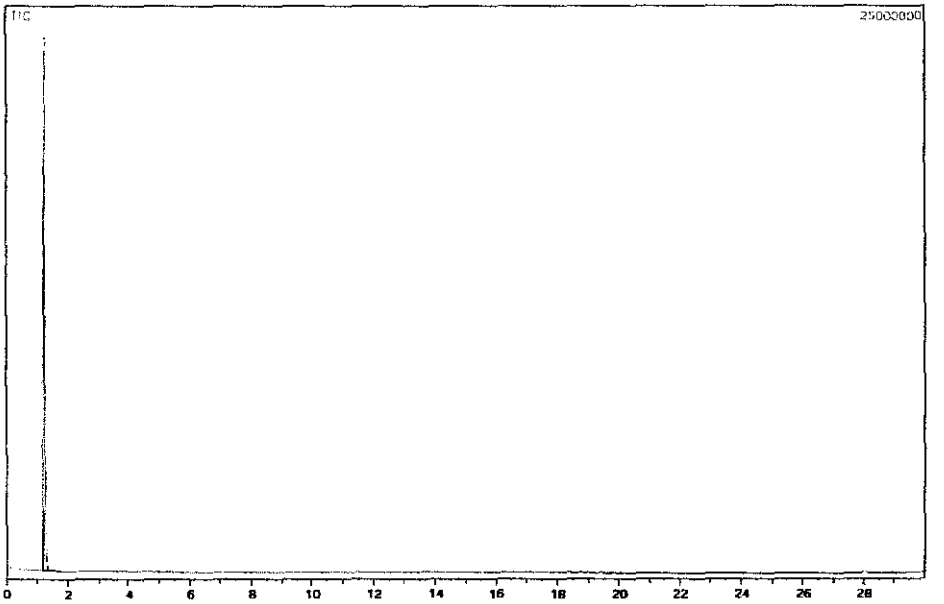

Figure 4.2: GC-MS analysis for biodiesel sample at 100°C.

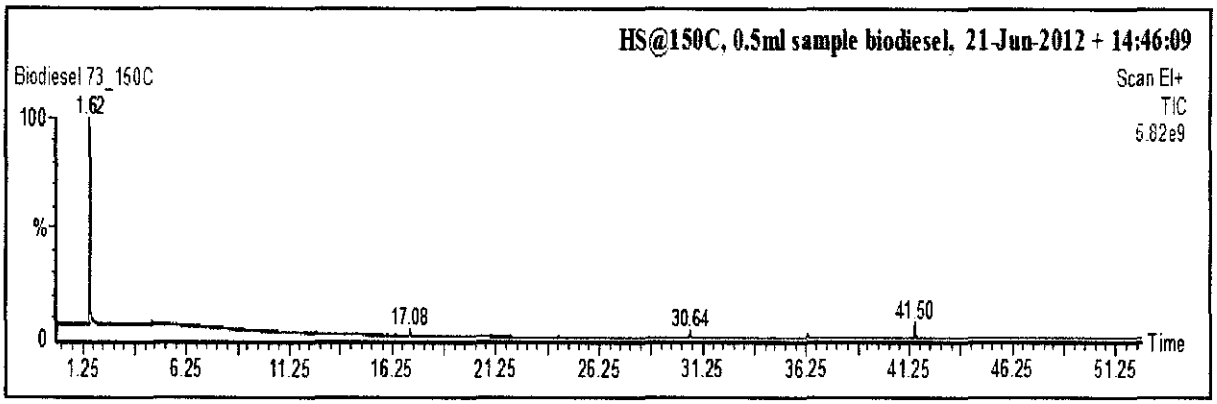

Figure 4.3: GC-MS analysis for biodiesel sample at 150°C.

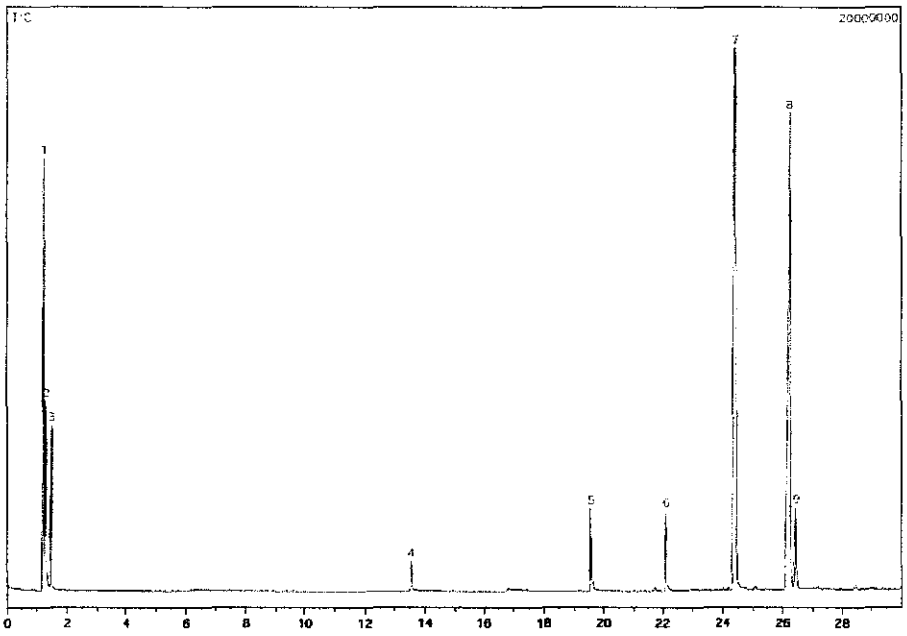

Figure 4.4: GC-MS analysis for biodiesel sample at 200°C.

Table 4.1: GC-MS components for biodiesel at 150°C

No	RT (min) GC-MS	Components	Molecular Formula
1	17.09	Methyl octanoate	$C_9H_{18}O_2$
2	30.64	Methyl dodecanoate	$C_{13}H_{26}O_2$
3	41.50	Methyl palmitate	$C_{17}H_{34}O_2$

Table 4.2: GC-MS components for biodiesel at 200°C

No	RT (min) GC-MS	Components	Molecular Formula
1	13.556	Methyl octanoate	$C_9H_{18}O_2$
2	19.609	Methyl dodecanoate	$C_{13}H_{26}O_2$
3	22.111	Methyl tetradecanoate	$C_{15}H_{30}O_2$
4	24.434	Methyl palmitate	$C_{17}H_{34}O_2$
5	26.252	Methyl oleate	$C_{18}H_{34}O_2$
6	26.445	Methyl stearate	$C_{19}H_{38}O_2$

4.2.1 Mole Fraction in Liquid Phase

Figure 4.5 and Figure 4.6 and Table 4.3 and Table 4.4 show the result distributions GC-MS for the mole fraction in liquid phase, x_i for each component in the liquid phase at 150°C and 200° respectively. Mass fraction of each component is calculated by dividing the individual peak area of each component with the total peak areas from GC-MS data. Then the mole fraction for each component is calculated using Equation (3-2).

Table 4.3: Different components present in the liquid phase at 150°C

No.	R_T (min) GC-MS	Compound	Formula	Bp oC	M_i	Area (Abundance)	Mass Fraction, xi	x_i/M_i	Mole Fraction xi (vol%)
1	17.09	Methyl octanoate	$C_9H_{18}O_2$	193.1	158.24	8923488	0.252	0.00159	34.90
2	30.64	Methyl dodecanoate	$C_{13}H_{26}O_2$	267.0	214.34	7489325	0.211	0.00099	21.62
3	41.5	Methyl palmitate	$C_{17}H_{34}O_2$	417.2	270.45	18998486	0.537	0.00198	43.48
Total						35411299	1	0.00456	100

Table 4.4: Different components present in the liquid phase at 200°C

No.	R_T (min) GC-MS	Compound	Formula	Bp oC	M_i	Area (Abundance)	Mass Fraction, xi	x_i/M_i	Mole fraction xi (vol%)
1	13.56	Methyl octanoate	C9H18O2	193.1	158.24	2621568	0.015	0.00010	2.63
2	19.61	Methyl dodecanoate	$C_{13}H_{26}O_2$	267.0	214.34	6329796	0.037	0.00017	4.69
3	22.11	Methyl tetradecanoate	$C_{15}H_{30}O_2$	323.0	242.40	6497883	0.038	0.00015	4.25
4	24.45	Methyl palmitate	$C_{17}H_{34}O_2$	417.2	270.45	80993288	0.468	0.00173	47.51
5	26.26	Methyl oleate	$C_{18}H_{34}O_2$	351.4	296.49	70315804	0.407	0.00137	37.63
6	26.45	Methyl stearate	$C_{19}H_{38}O_2$	443.0	298.51	6195345	0.036	0.00012	3.29
Total						172953684	1	0.00364	100

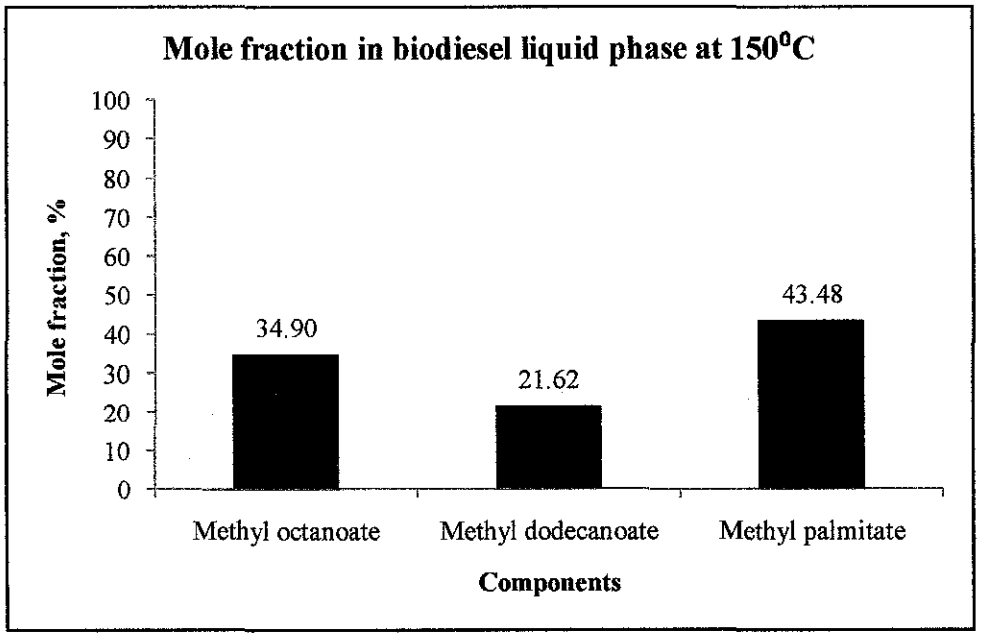

Figure 4.5: Mole fraction of biodiesel in liquid phase at 150°C.

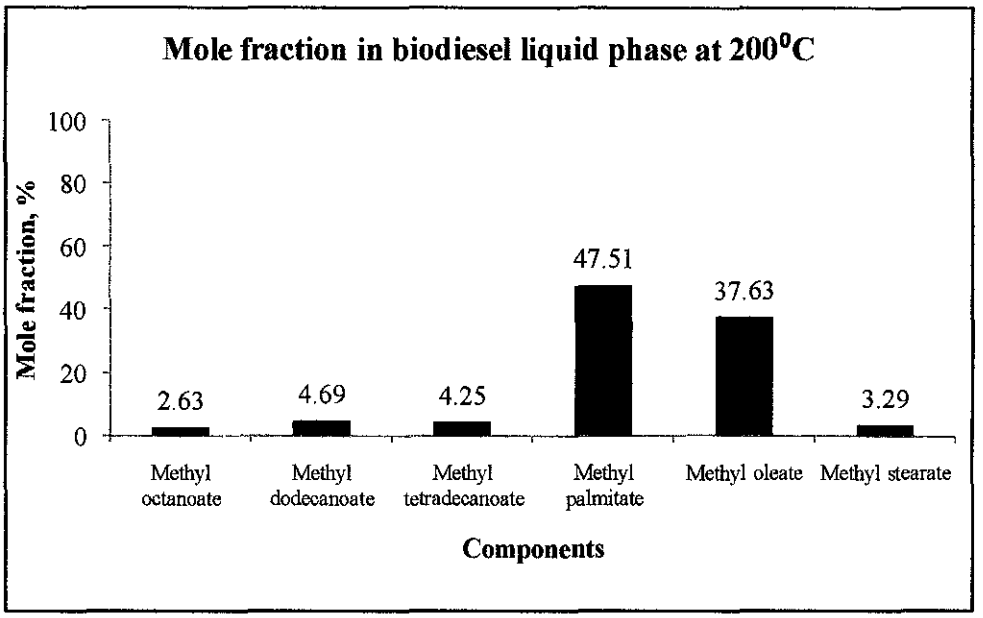

Figure 4.6: Mole fraction of biodiesel in liquid phase at 200°C.

4.2.2 Mole Fraction in Vapor Phase

Mole fraction in vapor phase is calculated using modified Raoult's Law (Eq. 3-4) which requires vapor pressure, the activity and fugacity coefficients of each component. Vapor pressure for each component was calculated using Antoinne equation (Eq. 3-5). All the constant values were obtained from Antoine Equation and Coefficients for Organic Compounds table from Yaws' Handbook of Antoine Coefficients for Vapor Pressure (2nd Electronic Edition) available in knovel.com. The activity coefficients were calculated using COSMO software while fugacity coefficients were identified from ThermoSolver software which is follows the Peng Robinson method by inserting all the critical properties and acentric factors for each component. Figure 4.7 and figure 4.8 display the mole fraction for each component in the vapor phase at 150°C and 200°C.

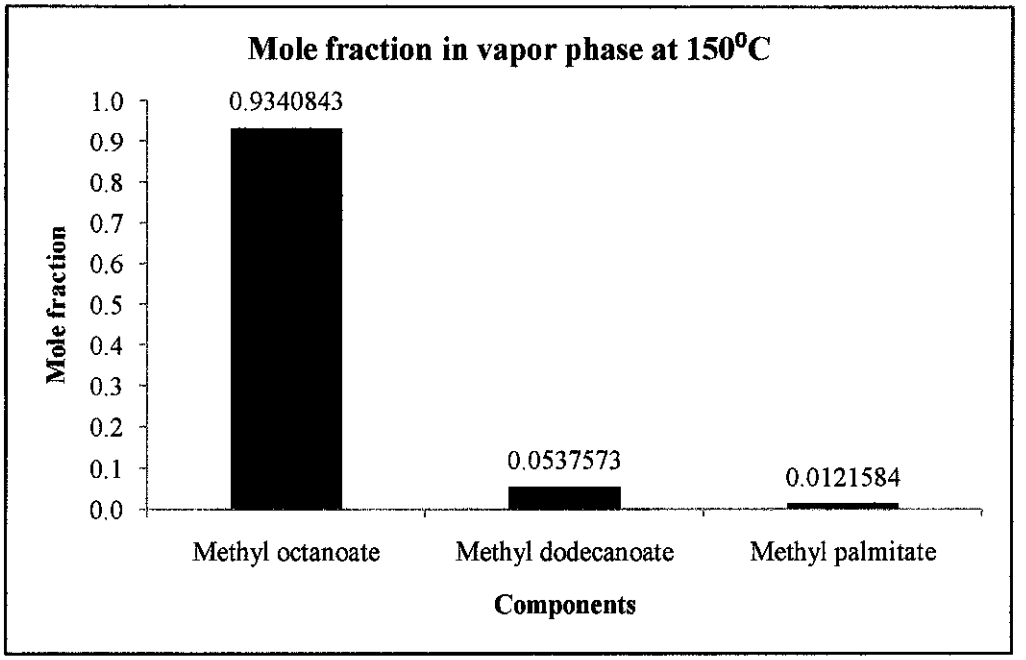

Figure 4.7: Mole fraction of biodiesel in vapor phase at 150°C.

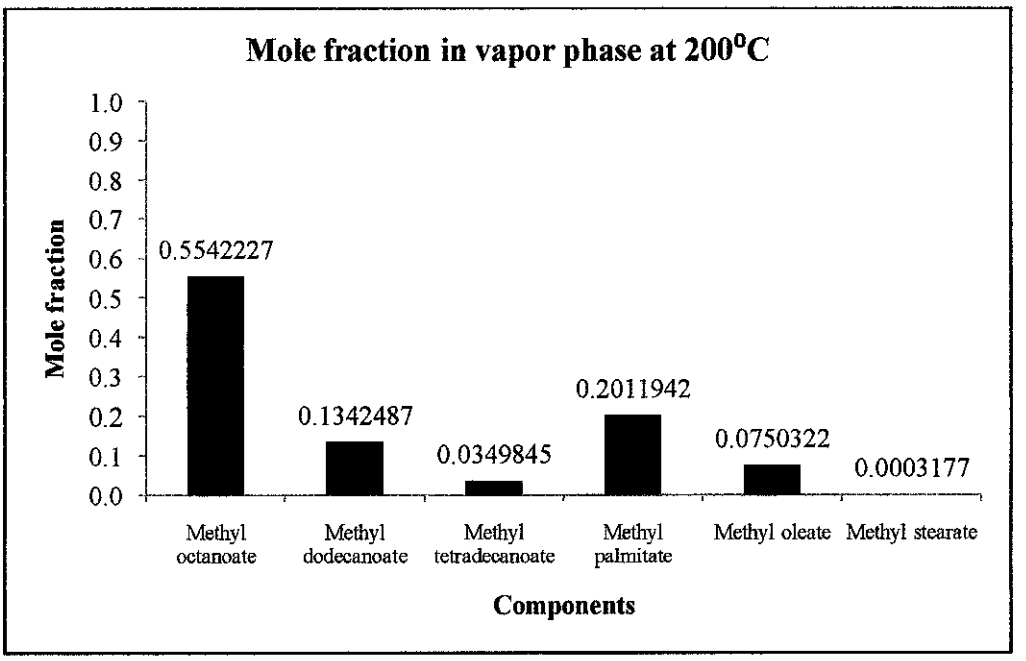

Figure 4.8: Mole fraction of biodiesel in vapor phase at 200°C.

4.3 LFL and UFL

The standard values of LFL and UFL at ambient temperature for each component in the vapor mixture have been calculated as a function of the stoichiometric

concentration C_{st} of fuel proposed by Jones, (1938) and given by Eq. (3-11) and Eq. (3-12). Since the objective of this study is to investigate the effect of temperatures on the flammability of biodiesel, the flammability limits changed with the temperatures. LFL and LFL for each component exist at different temperatures were calculated using Eq. (3-13) and Eq. (3-14) as proposed by (Zabetakis et al, 1959). The results are as tabulated in Table 4.5 and Table 4.6 for 150°C and 200°C respectively. The standard flammability limit values were compared with others obtained from experimental works and different published literatures. The results of LFL and UFL show that the calculated values are in fair agreement with those obtained from literatures with only slightly different. LFL_{mix} and UFL_{mix} for the vapor mixture were calculated according to Le Chatelier equation as given in Eq. (3-15) and (3-16).

4.4 Limiting Oxygen Concentration

LOC for given components in the vapor mixture is calculated using better estimated formula by Hansen and Crowl (2010) given in Eq. (3-17) and the results are presented in Table 4.5 and Table 4.6. The LOC_{mix} was found to be 11.92 vol% and 12.07 vol% at 150°C and 200°C respectively. The LOC_{mix} value is important in constructing the flammability diagram.

4.5 Flammability Diagram

A general way to represent the flammability of a gas or vapor is by the triangle diagram or flammability diagram. Concentration of fuel (biodiesel vapor mixture in this study), oxygen and inert material (usually nitrogen) are plotted on the three axes. To plot the flammability diagram, concentrations of fuel, oxygen and inert material (in volume or mole %) are required. Air line is plotted by taking the composition from Table 4.5 and Table 4.6. The stoichiometric line represents all stoichiometric combination of fuel plus oxygen. The intersection of the stoichiometric line with the oxygen axis (in volume % oxygen) is given by 100(z/1+z) (Crowl & Louvar, 2002). The LOC_{mix} line can be drawn by locating LOC_{mix} value on the air axis, then draw a parallel line until it intersects with the stoichiometric line.

To plot the flammability zone, the values of LFL_{mix} and UFL_{mix} are required. The LFL_{mix} and UFL_{mix} values are located on the air line, and then the flammability zone is considered the only area to the right of the air line. Figure 4.9 and Figure 4.10 represent the above procedure to generate the flammability diagram of biodiesel vapor mixture at 150°C and 200°C respectively using the result from Table 4.5 and Table 4.6. From the flammability diagram, it can be clearly visible that the stoichiometric line has crossed and lied in the flammability zone. Therefore it can be concluded that the biodiesel is flammable at higher temperature which is 150°C and 200°C.

Table 4.5: Compounds names and their relevant properties to estimate the flammability properties at 150°C

No.	R_T (min) GC-MS	Compound	Formula	Mole Fraction xi (vol%)	LFL (vol.%)		UFL (vol.%)		p^{sat} (mmHg)	Activity Yi	Fugacity Øi	y_i(vol%)	y_i(%)	y_i/LFL_i	y_i/UFL_i	z	UFL_o	LOC_i(%)	z/(1+z)	$\sum y_i*z$	$\sum(y_i*z)/L$
					std	150°C	std	150°C													
1	17.09	Methyl octanoate	$C_9H_{18}O_2$	34.90	0.9091	0.9090	5.7851	5.7852	216.7427	1.1448923	0.9404	12.1176	0.9341	1.0275	0.1615	13.5	19.7851	11.8818	93.103	12.6101	1.061
2	30.64	Methyl dodecanoate	$C_{13}H_{26}O_2$	21.62	0.6176	0.6175	3.9299	3.9300	20.4081	1.0574702	0.8805	0.6974	0.0538	0.0870	0.0137	19.5	20.1747	12.1158	95.122	1.0483	0.086
3	41.5	Methyl palmitate	$C_{17}H_{34}O_2$	43.48	0.4676	0.4676	2.9757	2.9757	2.2428	1.0114269	0.8227	0.1577	0.0122	0.0260	0.0041	25.5	20.3751	12.2361	96.226	0.3100	0.025
Total				100	**1.9943**	**1.9941**	**12.6907**	**12.6909**	**239.39**	**3.2138**	**2.6436**	**12.9727**	**1.0000**	**1.1405**	**0.1792**		**60.3349**	**36.2336**	**284.45**	**13.9684**	**1.173**
Average										**1.0713**	**0.8812**								**94.817**		

	(vol. %)
Results Summary	**150°C**
LFL_{mix}	0.8768
UFL_{mix}	5.5795
LOC_{mix}	11.9067
Stoichiometry	94.8173
Air	87.0273
N_2 = (79%)	68.7516
O_2=(21%)	18.2757

Table 4.6: Compounds names and their relevant properties to estimate the flammability properties at 200°C

No.	R_T (min) GC-MS	Compound	Formula	Mole fraction xi (vol%)	LFL (vol.%)		UFL (vol.%)		P^{sat} (mmHg)	Activity Yi	Fugacity Øi	y_i(vol%)	y_i(%)	y_i/LFL_i	y_i/UFL_i	z	UFL_o	LOC_i(%)	z/(1+z)	$\sum y_i*z$	$\sum(y_i*z)/LO$
					std	200°C	std	200°C													
1	13.56	Methyl octanoate	$C_9H_{18}O_2$	2.63	0.9091	0.9090	5.7851	5.7852	913.8638	1.1449	0.9404	3.8479	0.5542	0.6096	0.0958	13.5	19.7851	11.8818	95.1034	7.4820	0.6297
2	19.61	Methyl dodecanoate	$C_{13}H_{26}O_2$	4.69	0.6176	0.6175	3.9299	3.9300	125.8905	1.0575	0.8805	0.9321	0.1342	0.2174	0.0342	19.5	20.1747	12.1158	95.1220	2.6178	0.2161
3	22.11	Methyl tetradecanoa	$C_{15}H_{30}O_2$	4.25	0.5322	0.5322	3.3869	3.3869	43.3414	0.9343	0.9330	0.2429	0.0350	0.0657	0.0103	21.5	20.2888	12.1842	95.5556	0.7522	0.0617
4	24.45	Methyl palmitate	C_1-$H_{34}O_2$	47.51	0.4676	0.4676	2.9757	2.9757	18.1744	1.0114	0.8227	1.3969	0.2012	0.4303	0.0676	25.5	20.3751	12.2361	96.2264	5.1305	0.4193
5	26.26	Methyl oleate	$C_{18}H_{34}O_2$	37.63	0.4246	0.4246	2.7023	2.7023	9.0916	0.9665	0.8351	0.5209	0.0750	0.1767	0.0278	28	20.4325	12.2706	96.5517	2.1009	0.1712
6	26.45	Methyl stearate	$C_{19}H_{35}O_2$	3.29	0.4170	0.4169	2.6535	2.6536	0.4274	0.9974	0.8374	0.0022	0.0003	0.0008	0.0001	28.5	20.4428	12.2767	96.6102	0.0091	0.0007
Total				100	**3.3681**	**3.3677**	**21.4334**	**21.4338**	**1110.7892**	**6.1121**	**5.2491**	**6.9429**	**1.0000**	**1.5005**	**0.2358**		**121.4990**	**72.9652**	**573.1693**	**18.0924**	**1.4987**
Average											**0.8749**								**95.5282**		

	(vol. %)
Results Summary	**200°C**
LFL_{mix}	0.6665
UFL_{mix}	4.2411
LOC_{mix}	12.0717
Stoichiometry	95.5282
Air	93.0571
N_2 = (79%)	73.5151
O_2=(21%)	19.5420

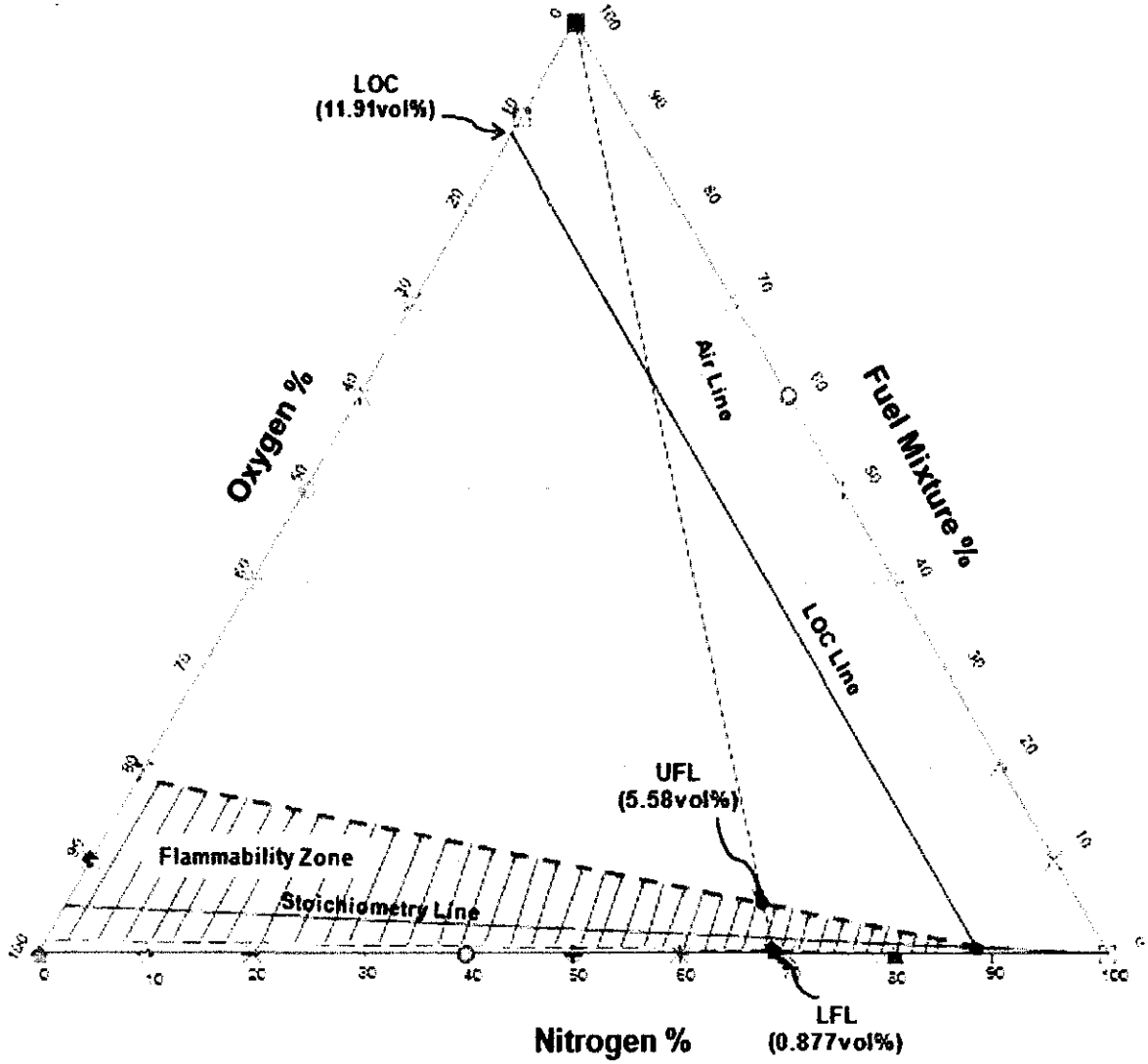

Figure 4.9: Flammability diagram of biodiesel at 150°C.

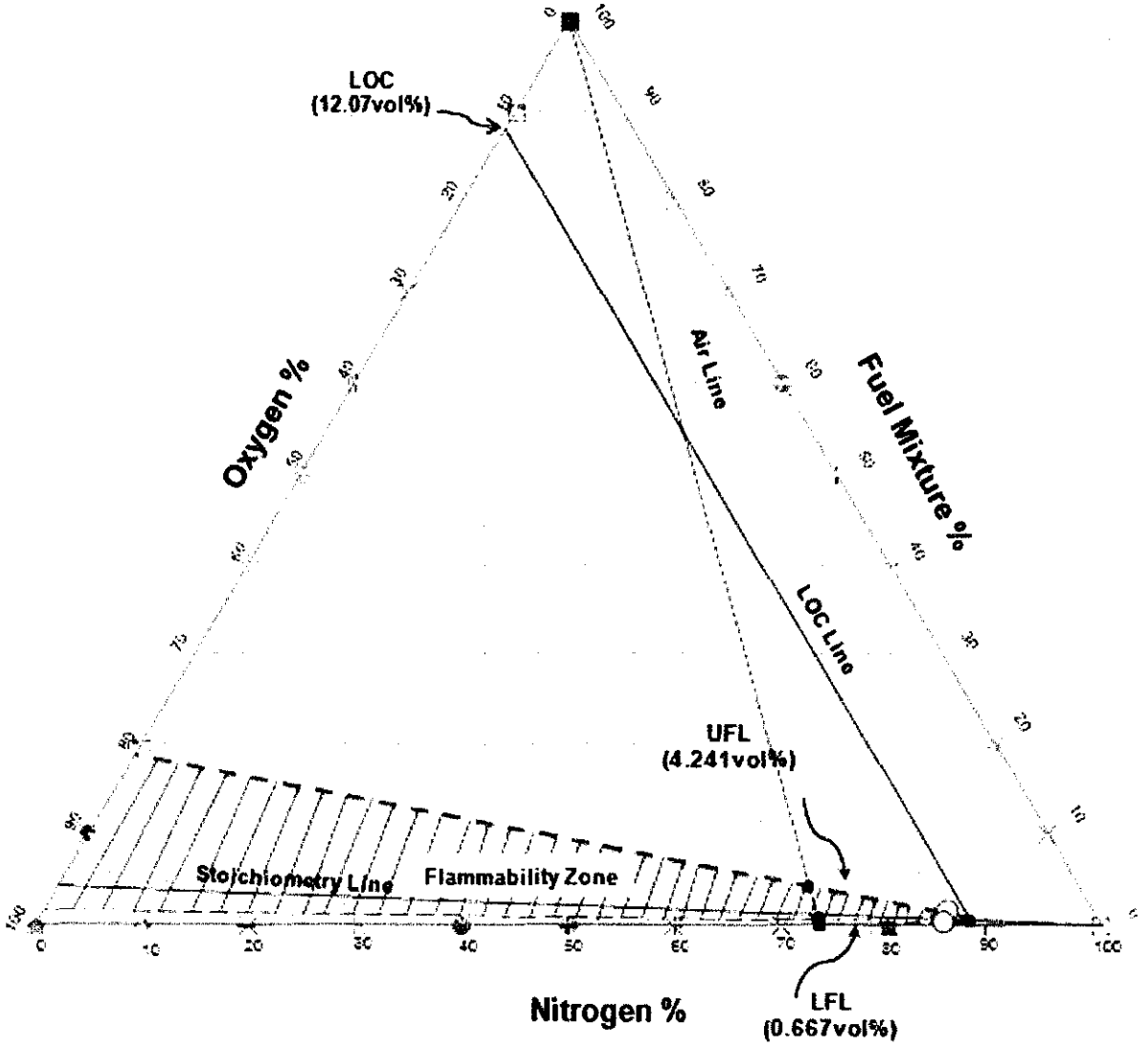

Figure 4.10: Flammability diagram of biodiesel at 200°C.

4.6 Inherent Safety

Flammable liquids will ignite and burn easily than combustible liquids at normal working temperatures. On the other hand, combustible liquids can burn when their temperatures increasing above working temperatures. This indicates that the flammable liquids are considered to be more hazardous than the combustible liquids. Accident histories show that most cases of fire involve flammable liquids. Flammable liquids do not burn by itself. Instead it will form vapors, which are highly flammable. The vaporization of a liquid depends on its temperature and vapor pressure. The warmer the liquid or the higher the temperature that the liquid is

exposed to, the more potentially hazardous it becomes. The flammability of a liquid depends on the degree to which the liquid forms flammable vapors. It should be noted that flammable liquids burn more readily and fiercely when the surrounding has a greater amount of oxygen (>21%) than that in the air.

At room temperature, some flammable liquids can give off enough vapors to form burnable mixtures with air. Therefore, the flammable components need extra precautions to be taken to minimize the possibility of fire. It is favorable to keep the mixture concentration below the LFL to avoid forming flammable mixture. On the other hand, combustible liquids at temperature above their flash point will also release enough vapor to form burnable mixtures with air. Combustible liquids at high temperature can be as serious as flammable liquids to cause fire. Flammable liquids should be prevented from spilling from the storage systems and production processes. Precautions need to be taken to prevent ignition of flammable vapors through the control of ignition sources such as open flames, lightning, hot surfaces, radiant heat, smoking, cutting and welding, static electricity, electrical sparks and stray currents, heating equipment. Furthermore, storage systems and production processes should be designed in such way to avoid flammable liquids accumulation. Accumulating of flammable liquids in the storage systems will increase the possibility of forming flammable vapors. Therefore, flammable liquids should be flushed and removed before entering storage systems.

The flammable and combustible liquids are present in almost every industry and workplace. If spill and leak occur in storage system, the vapors can spread from storage system to the vicinity areas. In presence of any ignition source and enough oxygen, these vapors can burn and cause fire.

From the results presented in this study, the following recommendations can be made to prevent fire from occurring by flammable vapors:

- Operation at less than the LFL is often considered to be safer than operation at above the UFL.
- Storage systems should be design to operate at lower temperature to avoid the vaporization of flammable mixture. The recommended conditions are at ambient temperature and atmospheric pressure.

- Eliminate ignition sources from areas where flammable vapors may be present in the storage systems and production process areas.
- Implement systematic hazardous material inventory especially for bulk storage and production of biodiesel. Ensure that the storage and production amount is proportional to the demand in avoiding the hazard potential.
- Samples should be frequently taken from the storage systems or production process areas and to be analyzed to confirm the flammability levels.
- Flammable and combustible waste should be drained away any accidental spillage to a safe, designated containment facility.
- Provide good ventilation for the storage systems and production process areas to dilute the flammable gas to a concentration below the LFL and then to prevent the accumulation of flammable vapors.
- Design a proper earthing, grounding and bonding system to avoid electrostatic hazards to the biodiesel storage systems and production processes.
- Design a proper layout of biodiesel storage systems and production processes. The good design should have adequate spacing and separation for the arrangement of biodiesel tanks, containers and other equipments.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This study is aiming to investigate the flammability of biodiesel at different range of temperatures vary from 50°C to 200°C at atmospheric pressure. Finding from this study will be used in proposing a systematic and safer approach to handle biodiesel storage systems and production process areas.

In this study, it covers both experimental and theoretical work. Experimental work involved production of biodiesel liquid sample and analyzing that sample using Gas Chromatography Mass Spectroscopy (GC-MS) to identify all the components exist in biodiesel and their composition. Theoretical work including thermodynamics fundamental and flammability calculations were applied to estimate the flammability of vapor mixture derived from biodiesel liquid. The GC-MS results indicated that there are no components vaporized from biodiesel liquid sample at lower temperature; 50°C and 100°C and at higher temperatures; 150°C and 200°C some components vaporized from biodiesel varying from C_9 to C_{19}.

To estimate the flammability of the vapor mixtures, mole fraction in vapor phase, y_i must be identified. Modified Raoult's law has been used in order to calculate this y_i value since this solution is found to be non-ideal. Simulation works has been applied to determine the value of activity coefficient; using COSMO software and fugacity coefficient; using Peng-Robinson method from Thermosolver software. Then Excel spreadsheets will be used calculate all the required data; LFL, UFL and LOC for each component and for the mixture at different temperatures. Later these data were used to construct the flammability diagram to determine the flammability of biodiesel liquid sample.

Based on the results obtained, biodiesel is not flammable and will not generate fire at lower temperature ; 50°C and 100°C since no components vaporized

at those temperatures. But as the temperatures increased to 150°C and 200°C, more components vaporized from biodiesel liquid sample. Based on the flammability diagram constructed at 150°C and 200°C, it can be clearly said that biodiesel is flammable at those temperatures and will generate fire if exposed to ignition sources and enough oxygen.

From this result, inherent safer design were proposed and discussed. This safety approach can provide useful guidelines to prevent build up of flammable mixtures that could lead to fire and explosions. Finally the findings of this study may contribute to minimizing the loss of properties, business and lives due to fire accidents. Hence, it can be concluded that the objectives of this study is achieved.

5.2 Recommendations

It should be noted that when all the necessary actions have been taken to evaluate the root cause of fire and explosion incident, the hazards shall be controlled and minimized accordingly as to avoid recurrence. Therefore, industrial should approach more preventive strategy such as the concept of inherent safety methods for their facility as recommended below:

1) Proper Plant Layout Design

   Safe plant layout designed based on standard design and local regulation. The right spacing of unit operations are critical so that there is adequate evacuation access in time of emergency especially during maintenance, shut down act and routine operation work which may involved a lot of hot work activities.

2) Elimination of ignition sources

   Ignition sources such as welding shall not be conducted near the storage system and production process areas if there is no O_2 content indication applied prior to hot work activities. As biodiesel storage systems and production process areas may contain traces of organic components which can vaporize to the surrounding.

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